ECOSAT

User manual

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M.G. Keizer

W.H. van Riemsdijk

Department of Soil Quality

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ECOSAT

A computer program for the calculation of

Speciation and Transport

in soil-water systems

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M.G. Keizer & W.H. van Riemsdijk

Department of Soil Quality
Wageningen University
P.O. Box 47
6700 AA Wageningen
The Netherlands

WAGENINGEN UNIVERSITY

WAGENINGEN UR

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1 Introduction

ECOSAT (acronym for Equilibrium Calculation Of Speciation And Transport) is a computer program which can be used to calculate the chemical equilibrium composition of soil-water systems, depending on speciation and transport . With speciation we mean the distribution of total amounts of components in the system over all possible phases and forms, including complexes, gases, minerals, organic liquids (pure organic compounds or (D)NAPL's) and adsorbed components. Besides speciation, ECOSAT can compute 1-dimensional and semi 2- or 3-dimensional stationary water or gas flow (**multi component transport**). Both speciation and transport calculations can include slow mass transfer (**reaction kinetics**).

For theoretical background of the processes involved reference is made to the course Soil Chemical Applications at Wageningen University.

The soil-water system description in ECOSAT is based on the use of different groups of variables :

Components :	basic entities used to form dissolved species, gases, minerals, organic liquids.
Particle surfaces :	used to define adsorption of components on the surface sites (surface components) in the form of surface species.
Environment :	ionic strength, temperature and gas volume.

In ECOSAT you can build your own system with these variables. You can add or edit the specific data in so called *edit tables*. A lot of the data needed can be selected from database files. Much attention has been given to an user friendly input and output interface.

The ECOSAT project on developing a speciation model started already in 1980 by the implementation of MINEQL (Westall;1976). Addition of sorption models - variable charge models (Basic Stern, Diffuse Double Layer, Constant Capacitance, Triple layer) and non-variable charge (Freundlich, Langmuir, Ion-exchange) - made the speciation model much more useful for specific applications in the field of soil chemistry and soil pollution.
Since then much work has been done on more sophisticated models for the description of sorption of ions to clay's, oxides and organic matter (sorption models including surface heterogeneity, e.g.), on multi component transport models and on slow mass transfer (reaction kinetics : e.g. slow decay, decomposition, desorption, dissolution) and on transport in the gas phase (e.g. important for volatile organic compounds in case of bioventing).
Speciation calculations were combined with slow reaction kinetics and transport. Together with the FIT-program (Kinniburgh, 1993) it is know possible to optimize a large number of model parameters.

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1.1 Installation

To start working with ECOSAT for the very first time you have to copy all files to your hard disk using the installation program: INSTALL.bat

The installation procedure creates the directory ECOSAT on your hard disk (ca. 4 Mb). Read the READ.ME file for the latest information.

ECOSAT is a DOS program, which runs in a DOS-window on a Windows-PC.
Make by yourself a short cut to your pc-desktop (icon) for ECOSHELL.exe.

1.2 Program structure

The ECOSAT package consists of 4 different programs, all related to each other :

Input manager : ECOSAT
Calculation program : ECOCALC
Output manager: OUTMAN
Windows shell : ECOSHELL

ECOSAT is the user input interface to compose and edit your own system. Data is stored in file *.ECO.
ECOCALC is the main program doing the calculations, reading data from file *.ECO. Output results are stored in file *.ECO at the end of the system description.
OUTMAN is the user output interface which can be used to select specific output results. Data from file *.ECO are read and used to make the selected output which is saved in file OUTMAN.DAT (see figure 1).
To facilitate working with ECOSAT in a Windows environment you can run ECOSHELL.exe.

These programs can run independently when their input files are available :

ECOSAT	run:	ECO.bat (last *.ECO file as default input)
OUTMAN	run:	OM.bat (last *.ECO file as default input)
ECOCALC	type :	ECOCALC *.ECO (*.ECO as input file); only in DOS environment.
ECOSHELL	run:	double click short cut (icon) on your desktop (see figure 2)

* : file name (maximum of 8 characters)

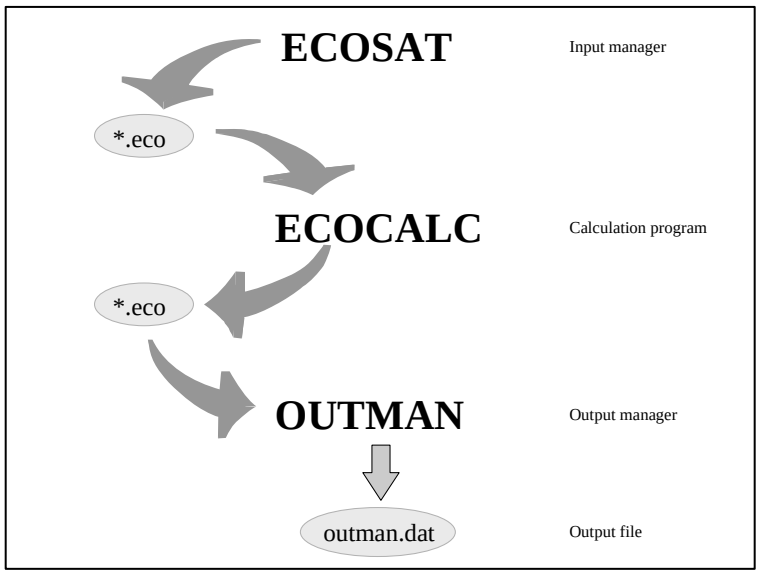


Figure 1. ECOSAT program and file structure

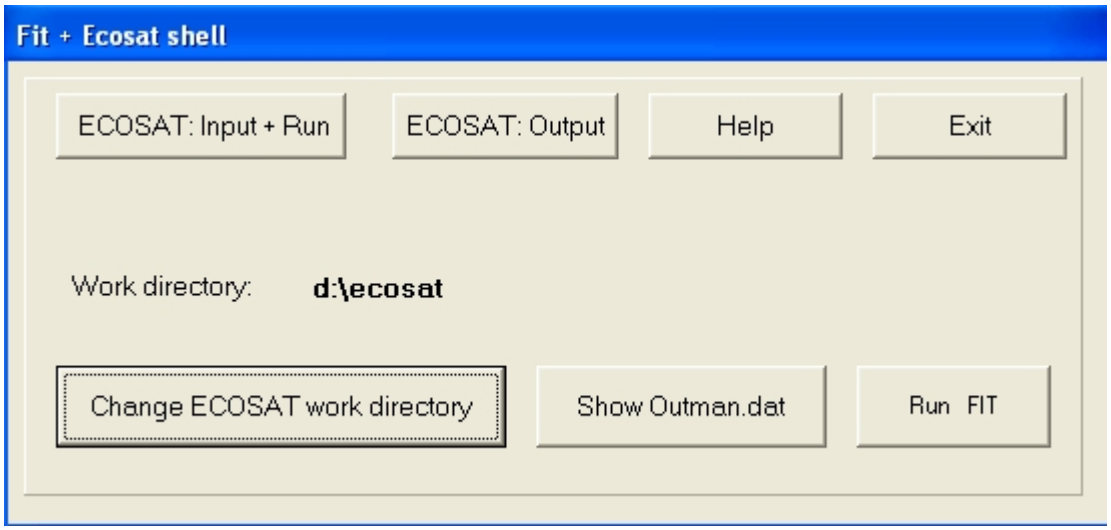


Figure 2. Start-up screen of ECOSHELL, a Windows shell for ECOSAT. Click on button ***ECOSAT: Input + Run*** for input of system data and starting the calculation (actually you start then ECO.bat). Click on button ***Show Outman.dat*** for displaying, printing or saving the calculated output in file OUTMAN.dat. Click on button ***ECOSAT: Output*** to generate output in file OUTMAN.dat (actually you start then OM.bat). With ***Help*** you get some more detailed information about this Ecosat shell. With button ***Change ECOSAT work directory*** you can change the (sub)directory in which you want to save the files. Button ***Run Fit*** starts the parameter fitting program FIT (see chapter 2.1.14).

1.3 Getting started :

To run the ECOSAT program in a Windows environment, double click ECOSHELL.exe (make an icon on your desktop) and click on button ***ECOSAT: Input + Run (*** see figure 2).

To run the ECOSAT program in a DOS environment, type : ECO

ECO.BAT is a batch file with respectively the commands :

```
ECOSAT
ECOCALC  *.ECO
OUTMAN
```

ECOSAT creates an user input data file : *.ECO (* = user name).
This data file contains the system description (components, species, etc.). The results of a successful calculation are added at the end of this file. Run-time errors are reported in file ECOSAT.LOG.

The output manager (OUTMAN) reads file *.ECO, and creates after output selection the file OUTMAN.DAT with the selected output ordered in columns (menu option CHOICE) or all basic output (unchanged data saved by ECOCALC) in sequential order (menu option BASIC or ALL). The column ordered output file can easily be imported into a spreadsheet program.

To run the output manager in a Windows environment, click button *ECOSAT: Output* in ECOSHELL (see figure 2)**.**

To run the output manager in a DOS environment, type : OM

OM.BAT is a batch file with the command OUTMAN.
See chapter 3 for detailed information.

1.4 ECOSAT edit tables

System description is specified in so called *edit tables* (saved in *.tmp files in subdirectory ./ecotmp) There are edit tables for all different groups of variables such as : components, species, gases, minerals, organic liquids, particle surfaces, surface components, surface species, environment (ionic strength, temperature, gas volume), for PC- and program setup and for additional information used for the different calculation types :

Multiple run	:	e.g. titration or reading (measured) data from file
Cascade	:	repeated soil extraction
Kinetics	:	slow mass transfer
Transport	:	1-dimensional stationary water or gas flow; also semi 2- or 3-dimensional transport (using mathematical transformation to 1-dimensional transport; e.g. axial or radial symmetric flow).
Fit	:	parameter optimization with the program FIT (version 2.5).

In these tables input data can be specified for each variable or parameter in a separated table row. Data in the different columns represent specific formatted information for that variable (see figure 3).

Special function keys (see Help text (F1) for more information) :

F1	on-line help; help index
F2	Save the edit table and return to the ECOSAT main menu
F3	Save edit table and go back to previous menu
F4	Accelerator to PHASES menu
F5	Accelerator to ADSORPTION menu
F6	Accelerator to MULTIPLE RUN menu
F7	Accelerator to KINETICS menu
F8	Accelerator to TRANSPORT menu
Esc	Quit the edit table (do not save); Back to previous menu
Ins	Insert row in edit table
Del	Delete field in edit table
Alt Y	Delete row in edit table
Alt C	Copy row in edit table

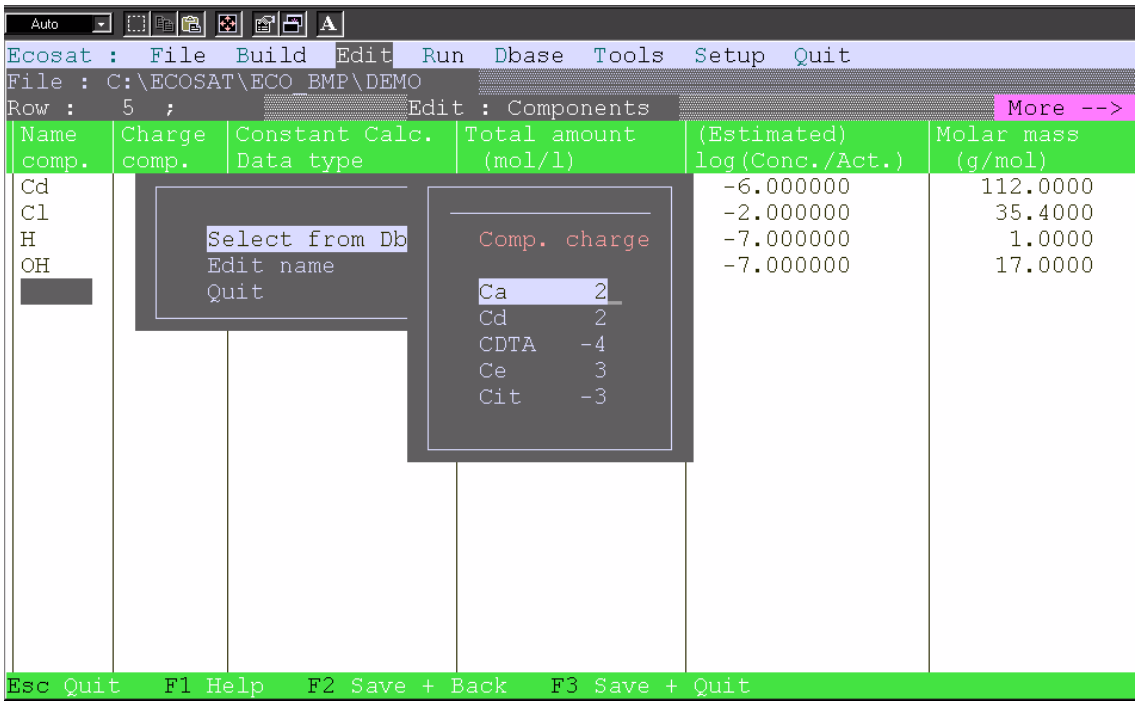


Figure 3. Components edit table in the ECOSAT input manager; selection from database.

The maximum number for most variables in the edit tables amounts 200 (maximum of 200 rows in the tables). However maximum amount of components and particle surfaces is limited to 25 (in the database 200). For each particle surface maximum number of surface components and surface species amounts respectively 15 and 75. Limits depend also on your computer memory.

The columns in the edit tables have all a specific format. Several format types are possible :

1 Select from menu
2 Select from data set
3 Integer value
4 Real value
5 Log (real) value
6 Character string
7 Unit choice for variable or parameter value
8 Toggle yes/no

The field width is an indication for the maximum number of characters that can be used (for type 3, 4, 5, 6 and 7). To find out which format for a column is applicable move the cursor to a field in a specific row and column, using arrow keys, and press key ENTER :

- For type 1 and 2 a window appears with several menu options or with a specific data set (e.g. all components present in the database). Use arrow keys to move and press ENTER to select.

  For selection of an item from the data set shown in the window you can also move the cursor to a certain item by typing the first character(s) of its name.

- For type 3, 4, 5, and 6 the cursor will move into the field and you can start editing. For those column format types it is not necessary to start editing always with ENTER. You can also directly start editing by typing the first character of the number or string. ECOSAT will check for the right format.

- For type 7 a window appears with several menu options. Use arrow keys to move and press ENTER to select. You can choose a certain unit and add then the variable or parameter value (e.g. mol/l or mg/l for the total amount of the component). ECOSAT will automatically recalculate this value into the standard (default) unit (e.g. mol/l).

- For type 8 the value in the field changes after pressing ENTER : Yes --> No and No --> Yes.

In most edit tables the first column is reserved for the name of the variable (e.g. component or species). The format of this column is of type 1, combined with type 2. In this case the available menu options are :

Select Item Select the variable from the specified database file : in a second window you can make a selection from the active database set. Not only the variable name, but also all other data specific for the chosen variable present in the other columns, is retrieved from the database file and added to the edit table.

Set Dbase file Select the active database file from a second window.

Edit name Edit the variable name (use this only if the variable name is not available from the database file). **Changing a component name is equal to deleting the old one and inserting a new one. This can mean that (surface) species become deleted !**

Quit Quit the window without making any selection (same as Esc).

2 Input manager

Start the program with **: ECO** (DOS) or click on button ***ECOSAT: Input + Run*** in ECOSHELL (Windows)**.**

The program begins with displaying the ECOSAT start screen. **Press any key to continue**. The next screen displays several menu options in the ECOSAT main menu and an overview of the system description. Use F1 to get on line help information anywhere in the program. In the second row at the left the actual file name (*.ECO) is shown.

ECOSAT main menu options (see also figure 4) :

File : File handling (retrieve, save, start a new file, etc.)
Build : Build your system by adding chemicals, minerals or organic liquids.
Edit : Change the edit tables
Run : Start calculation
Dbase : Edit database files
Tools : several extra facilities
Setup : PC and program parameter settings
Quit : Quit program (no calculation).

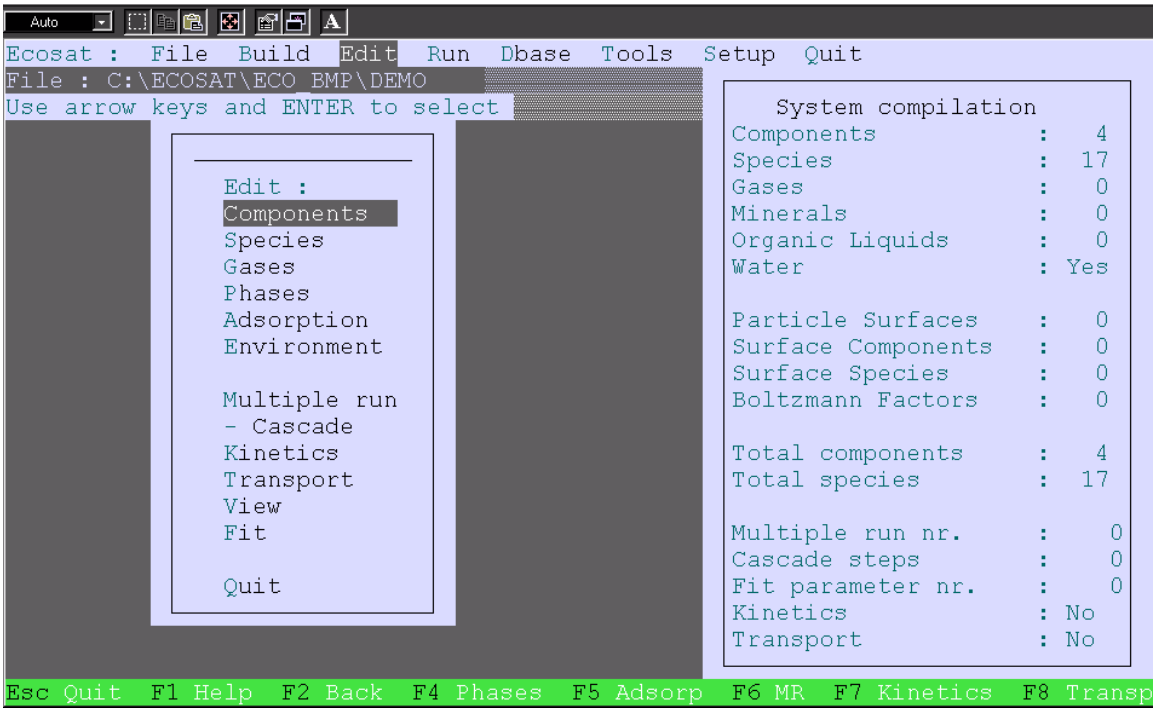


Figure 4. ECOSAT input manager : main and edit menu; system compilation.

To do an ECOSAT calculation you have to create your own chemical system using the available variable groups (e.g. components, particle surfaces, species, etc.). **Start always with defining the components.**
Use as much as possible the available database files for easy selection of the variables you need. If specific data is not present in the database files you can better add the new data immediately to the database file for later use. Of course it is always possible to add new data only to the edit tables.
It is also possible to make your system using added total amounts of chemicals, minerals or organic liquids. Use in that case menu option BUILD. ECOSAT selects automatically the components, species, etc. from the database files.

After selection of the variables present in the system you can define a certain calculation type :

- *Multiple Run* (Single Run = the default calculation type)
- *Cascade*
- *Kinetics*
- *Transport*
- *Fit : parameter optimization (combine with FIT.exe)*

If the system description is complete, select menu option RUN. The calculation starts then. The output manager OUTMAN will get started automatically when calculation is finished.
Don't make your system too complicated at the first time but try to run the program first with a rather simple system.
To create a complete new system go to menu option **FILE** and select option **NEW**. All edit tables will get cleared and you start with empty edit tables. Select menu options EDIT or BUILD to formulate your new system.

2.1 System description

See also appendix 1: Speciation calculations in ECOSAT.

2.1.1 Components

First of all you have to select the components which will be present in the system: select EDIT and then COMPONENTS in the edit menu. In the components edit table you have to fill in the *component names*, and further also data like : *constant calculation data type* (indicating what is constant: total amount, concentration or activity), *total amount*, (estimated) *concentration or activity* (log value), *charge* and *molar mass* (see also figure 3).

For each component only total amount ***or*** concentration **or** activity can be constant.

- If total amount is constant then **log(conc./act.)** has to be given as an **estimated** (starting) value. The equilibrium concentration will be calculated then.
- If concentration or activity is constant then **total amount** will be calculated: no input value for total amount is necessary (can be zero).

If total amount is *constant* (= known value; constant calc. data type = *'Total amount'* or *'P-gas -> Total amount'* or *'H2O -> Total amount'*) you have to give a positive value for the total amount of the component present. A total amount of zero means that the component is **not** present in the system for that calculation unless data type equals *'P-gas -> Total amount'* or *'H2O -> Total amount'.*
In case of zero total amount and constant calc. data type = *'Total amount'* all concentrations of (surface) species and phases containing this component are set to zero. For the components H and OH the program will automatically add the amount present in water (55.56 mol/l) for these two components. Therefore data type equals *'H2O -> Total amount'.*
The constant calculation data type can also be '*P-gas > Total amount'* which indicates that total amount is constant and (partly) determined by the constant gas pressure of the gas species containing the component.

It is possible and convenient to select all components from the database file. However it is also possible to add them directly into the components edit table. If you want to add components to the components database file select : DBASE - COMPONENTS - EDIT and edit the database file. This file has the default name ECOCOMP.dbA).
When all components are added to the edit table you have to save this components edit table: Quit and Save (press Esc or F2 or F3).
Species, gases, minerals, organic liquids, etc. can be added automatically from the database files to their respective edit tables depending on the settings of the database-auto-fill parameters (go to DBASE - DBASE GROUP - AUTO FILL; see chapter 2.2).

It is also possible to add components automatically to the system via menu option BUILD (see chapter 2.3). See chapter 2.1.9 for multiple run calculations with components total amount (e.g. titration) and/or components concentration or activity (e.g. pH range).

2.1.2 Species

The dissolved species in the system have to be defined in the species edit table (select EDIT - SPECIES). They will be added automatically from the database files after selection of the components if the database-auto-fill parameter for species is set to *Yes* (= default value; see chapter 2.2). In the edit table you can change or add/delete species data like : name, composition, delta H and log(K^o) values. Molar mass of the species will be calculated automatically by the program after saving the edit table.
All components, except *e* (electron) are added automatically to the species edit table. It is easy to select all other species from the database files. However it is also possible to add them directly into the species edit table. If you want to add species to the species database files select : DBASE - SPECIES - EDIT and edit the database files. When all species are added to the edit table you have to save this edit table : Quit and Save (press Esc or F2 or F3).
It is possible to optimize log(K^o) values for species with FIT + ECOSAT (EDIT-FIT; see chapter 2.1.13).

2.1.3 Gases

The gas species in the system have to be defined in the gases edit table (select EDIT - GASES). They can be added automatically from the database files after selection of the components if the database-auto-fill parameter for gases is set to *Yes* (which is not the default value !). The default setting of this database-auto-fill parameter is *No*. Selection of the components H, OH and *e* (electron) should always result in automatic selection of the gases H_2 and O_2. However, often you will not be interested in these gases. Therefore select the gases manually: press ENTER when the cursor is in the first column of the gases edit table and choose *Select Item* from the menu displayed in the window.
It is very easy to select all gases from the database files. If you want to add new gases to the gases database files select : DBASE - GASES - EDIT and edit the database files.

In the edit table you can change or add/delete gases data : name, composition, delta H, log(K_p), gas pressure type (*constant or variable*) and gas pressure (different units; e.g. bar or Pa). Molar mass of the gas species will be calculated automatically by the program after saving the edit table.
Log(K_p) equals here to the Henri constant in L.bar.mol^{-1}. Gas pressure is expressed in bar (default unit).

Two different calculation types for gas pressure are possible. Probably in most cases you want to do a single speciation calculation with a constant gas pressure (gas pressure type: *Constant*) or with a variable gas pressure (gas pressure type: *Variable*). For both situations you have to specify also the gas volume (=gas/liquid ratio) in the system (select EDIT - ENVIRONMENT). The components edit table will be checked for the chosen gas type. For multiple run calculations with constant gas pressures, see chapter 2.1.9.
When all gases are added to the edit table you have to save this edit table : Quit and Save (press Esc or F2 or F3).

2.1.4 Minerals

The minerals in the system have to be defined in the minerals edit table (select EDIT - PHASES - MINERALS). Relevant minerals can be added automatically from the database files if the database-auto-fill parameter has been set to *Yes* (which is not the default value !). For available standard database files for minerals, see chapter 2.2.
The default setting of the database-auto-fill parameter for minerals is *No*. The database files contain many minerals with the same chemical formula which cannot exist all together in the same system (phase rule violation). Therefore the default setting is aimed at selecting the minerals manually: press ENTER when the cursor is in the first column of the minerals edit table and choose *Select Item* from the menu displayed in the window.
In the edit table you can change or add/delete mineral data : name, composition, delta H and log(K_s) values. Molar mass of the minerals will be calculated automatically by the program after saving the edit table.

It is easy to select all minerals from the database files. However it is also possible to add them directly into the minerals edit table. If you want to add new minerals to the minerals database files select :

DBASE - PHASES - MINERALS - EDIT and edit the database files.
When all minerals are added to the edit table you have to save this edit table: Quit and Save (press Esc or F2 or F3). You can also add minerals to the system via menu option BUILD (see chapter 2.3).

2.1.5 Organic Liquids

The organic liquids (pure organic compounds or (D)NAPL's) in the system have to be defined in the organic liquids edit table (select EDIT - PHASES - ORG. LIQUIDS). Relevant organic liquids can be added automatically from the database file if the database-auto-fill parameter has been set to *Yes* (=default value).
In the edit table you can change or add/delete organic liquid data: name, delta H and log(S) values. Molar mass of the organic liquids will be calculated automatically by the program after saving the edit table.
It is easy to select all organic liquids from the database files. However it is also possible to add them directly into the organic liquid edit table. If you want to add new organic liquids to the database files select : DBASE - PHASES - ORG.LIQUIDS - EDIT and edit the database files.
When all organic liquids are added to the edit table you have to save this edit table: Quit and Save (press Esc or F2 or F3). You can also add organic liquids to the system via menu option BUILD (see chapter 2.3).

For mixtures of organic liquids Raoult's law is used to calculate the equilibrium concentration in the water phase (actual mole fraction times saturated water solubility) and gas phase (actual mole fraction times saturated vapour pressure). See also appendix 1.

2.1.6 H_2O

Water is present in the system if both H and OH are chosen as components. However the speciation calculations are mathematically possible even if water as separate phase is not present (H or OH is not a component).
Water is only partly treated in the same way as minerals and organic liquids. The difference is that the total amount of the components present in water (H and OH) have **NOT** to be added to the total amount of the components in the whole system.

If the constant calculation data type of component H or OH = *'Activity'* or *'Concentration'*, the constant calculation data type of the other component in water (OH or H) has to be *'Total amount' or better 'H2O -> Total amount' ;* otherwise you will encounter a phase rule violation. Total amount of both H and OH will then be calculated. With *'H2O -> Total amount'* we mean that total amount of component H or OH is constant and that the actual value will also be determined by water dissociation.

The total amount of components H and OH (constant calculation type = *'H2O -> Total amount'*) does not include the total amount present in water (= 55.56 mol/l at 25 ^{o}C). This value of 55.56 mol/l will be added automatically by the program (ECOCALC). Thus for H and OH, total amount in the components edit table can be zero, while they still are present !

Total amount for H and OH given by the output manager does NOT include this 55.56 mol/l !

In the H_2O-edit table (select EDIT - PHASES - H_2O) it is possible to change the dissociation constant of water.

2.1.7 Environment

The environment parameters ionic strength, temperature and gas volume have to be defined in the environment edit table (select EDIT - ENVIRONMENT).
Ionic strength is necessary to calculate the activity coefficients which will be used to convert component and species activity into concentration. ECOSAT uses a slightly adapted Davies equation for that purpose (see help text for detailed information). Parameters for the Davies equation can be set at SETUP.

Temperature can be used to calculate log(K^o) for dissolved species, gases, minerals and organic liquids at temperature T with the given log(K^o) at T = 298.15 K and delta H (enthalpy change) with the Van't Hoff equation**.**
Note: delta H values are not yet compiled in the database files (see HELP info for calculating delta H values) !

If gas pressure is variable, gas volume has to have a certain constant value. With this volume the partial gas pressure can be calculated. Also for a constant gas pressure a certain positive gas volume should be given, although this is not necessary to calculate the speciation. In this case the volume is only used to calculate the total amount of the components present in the system.

In case of a constant gas pressure total amount of the component(s) present in the gas species will be determined by the value of the partial gas pressure. If constant calc. data type of this component equals 'Total amount' it will be converted automatically into *'P-gas -> Total amount'*. It means that total amount of the component is constant and that its value is also determined by the partial gas pressure of the gas species.
See chapter 2.1.9 for multiple run calculations with constant ionic strength, temperature and gas volume.

2.1.8 Adsorption

The concept applied in ECOSAT to model adsorption and desorption of compounds is that this sorption takes place on (soil) particle surfaces according to a particular sorption model. Depending on the chosen model sorption is described with the aid of surface components (surface sites) and surface species (bound components on surface sites).

To describe sorption we need :

- a certain amount of a particle surface (kg/l).
- a sorption model describing sorption onto that particle surface, including the model parameters.
- a certain amount of surface components on the particle surface (mole/kg). Multiplied with the particle surface total amount this equals to the maximum binding capacity (mol/l) in the system.
- Surface species representing the bound components.

In ECOSAT different sorption models are available :

- Several non-variable charge (nvc) sorption models : Freundlich, Langmuir, Ion Exchange (Gaines-Thomas and Donnan).
- Heterogeneous sorption models like : NICA, Langmuir-Freundlich, Generalized Freundlich, Toth. These models can also be combined with electrostatic (variable charge) models.
- Several variable charge (vc) electrostatic models : Diffuse Double Layer (DDL), Constant Capacitance (CC), Basic Stern (BS), Three planes (TP) and Donnan. *These models can be applied for different geometry of the particle surfaces : plane (DDL, CC, BS, TP) or gel (Donnan).*
- Specific models like the Surface Precipitation Model (SPM).

To define sorption you have to add a certain amount of a particle surface into the system. Assign a specific sorption model to that particle surface and define all other variables and parameters you need to describe sorption: surface components (not for the Freundlich model), surface species and different model parameters.

2.1.8.1 Particle surfaces

The particle surfaces in the system have to be defined in the particle surfaces edit table (select EDIT - ADSORPTION - PARTICLE SURFACES). In the particle surfaces edit table you have to fill in the particle surface *name*, *particle type, total amount* and the relevant *sorption model*. Total amount can be related to the total amount of a mineral present in the system (*related mineral*).

It is possible to select all particle surfaces from the available database file. However it is also possible

to add them directly into the particle surface edit table. If you want to add particle surfaces to the database file select : DBASE - ADSORPTION - PARTICLE SURFACES - EDIT and edit the database file. This file has the default name ECOPART.dbP.

Surface components, surface species and model parameters can be added automatically to their edit tables depending on the setting of the database-auto-fill parameter (select DBASE - ADSORPTION - SURFACE SORPTION - AUTO FILL; see chapter 2.2). The default setting for this parameter is *Yes*.

The particle surfaces can be of type *Solid*, *Suspended* or *Biota*:
Suspended particles are subject to transport in the water phase: e.g. dissolved organic carbon (DOC) or oxide colloids. Uptake of components by soil organisms is simulated by adsorption. In that case choose for particle type *Biota* to distinguish uptake from normal adsorption. *Solid* is the default particle surface type.
Particle total amount (kg/l) can be set equal to the total amount of a mineral present. Select therefore a mineral in the column *Related Mineral*. Total amount of the mineral (mol/l) is converted into kg/l for the particle surface with the molar mass of the mineral. The total amount for the particle surface specified in this edit table is then an initial estimate for the iteration procedure. For maximum number of iteration steps and relative tolerance value (default 0.5 %) see Setup (§ 2.5).

ECOCALC converts total amount of the sorbed components (= surface species) from mol/kg into mol/l by adapting $\log(K_a)$ values to $\log(K_c)$ values. For nvc-models by using the particle surface total amount (kg/l) and total amount of the surface component (mol/kg) and for most vc-models by using the number of sites/nm^2, specific surface area (m^2/kg) (see model parameters) and particle surface total amount (kg/l).

Selection of sorption models occurs according to the following scheme
(press ENTER in the column *Sorption model*) :

Non-Variable Charge : - Freundlich
- Langmuir : - normal (1-site)
  - advanced (2-sites)
- Ion Exchange : - Gaines-Thomas
  - Donnan
- Heterogeneous : - NICA
  - CONICA
  - Langmuir-Freundlich
  - Generalized Freundlich
  - Toth

Variable Charge :
- Langmuir : - normal (1-site) > GM-VC
  - advanced (2-sites) > GM-VC
- Heterogeneous : - NICA > GM-VC
  - CONICA > GM-VC
  - Langmuir-Freundlich > GM-VC
  - Generalized Freundlich > GM-VC
  - Toth > GM-VC
- Surface Precipitation Model (SPM)

> GM -VC : choose geometry and charge model ;

Geometry
- plane
- gel

Charge models

- Diffuse Double Layer
- Constant Capacitance
- Basic Stern
- Three planes
- Donnan (only for gel geometry)

Examples of possible choices for the sorption model :

nvc	*- Freundlich*			
nvc	*- Langmuir*	*- normal*		
nvc	*- Ion-exchange*	*- Gaines-Thomas*		
nvc	*- Ion exchange*	*- Donnan*		
nvc	*- Heterogeneous*	*- NICA*		
vc	*- Langmuir*	*- normal*	*- plane*	*- Basic Stern*
vc	*- Langmuir*	*- advanced*	*- plane*	*- Diffuse double layer*
vc	*- Heterogeneous*	*- NICA*	*- gel*	*- Donnan*

See the help text (F1) for more detailed information about the sorption models.

When all particle surfaces are added to the edit table you have to save this edit table: Quit and Save (press Esc or F2 or F3).
After specifying particle surface data you have to define the surface components (not for Freundlich), surface species and model parameters : select EDIT - ADSORPTION - SURFACE SORPTION.

All variables (surface components and surface species) and all model parameters can be added automatically after saving this particle surface edit table if the database-auto-fill parameter is set to *Yes* (=default value; see chapter 2.2). Selection is based on particle surface **name**, sorption model and already defined normal components.

See chapter 2.1.9 for multiple run calculations with particle surface total amount (EDIT-MULTIPLE RUN). See chapter 2.1.13 for optimization calculations for particle surface total amount with FIT + ECOSAT (EDIT-FIT).

To edit the surface components, surface species or the model parameters: go to EDIT - ADSORPTION - SURFACE SORPTION and select the particle surface for which you want to edit the surface sorption data.

2.1.8.2 Surface components

All surface components present on the selected particle surface have to be defined in the surface components edit table: go to EDIT - ADSORPTION - SURFACE SORPTION - COMPONENTS (SURF.). Here the surface component name, and depending on the chosen sorption model several different parameters like total amount (mol/kg) or number of sites/m^2, charge and the heterogeneity parameter can be edited.

The surface components can be added automatically from the database file if the database-auto-fill parameter has been set to *Yes* (default value). It is very easy to select the surface components from the database file. However it is also possible to add them directly into the surface components edit table. If you want to add new surface components for this particle surface to the database files go to : DBASE - ADSORPTION - SURFACE SORPTION - COMPONENTS (SURF.) - EDIT and edit the database file. When editing is finished you have to save this edit table : Quit and Save (press Esc or F2 or F3).

See chapter 2.1.9 for multiple run calculations for several variables (EDIT-MULTIPLE RUN-SURFACE SORPTION-COMPONENTS). See chapter 2.1.13 for optimization calculations with FIT + ECOSAT (EDIT-FIT).

Note : *For the Freundlich sorption model no surface components are required !*

2.1.8.3 Surface species

All surface species present on the selected particle surface have to be defined in the surface species edit table: go to EDIT - ADSORPTION - SURFACE SORPTION - SURFACE SPECIES. Here the surface species name and composition, log(K_a) and depending on the chosen sorption model other parameters can be edited.
The surface species can be added automatically from the database file if the database-auto-fill parameter has been set to *Yes* (default value). It is very easy to select surface species from the database file. However it is also possible to add them directly into the surface species edit table. If you want to add new surface species for this particle surface to the database files go to: DBASE - ADSORPTION - SURFACE SORPTION - SURFACE SPECIES - EDIT and edit the database file. When editing is finished you have to save this edit table: Quit and Save (press Esc or F2 or F3).

For the Freundlich model Log(K_a) values of the surface species are adapted to log(K^c) values by ECOCALC using total particle surface amounts and the correction for ionic strength (only for the dissolved components present in the sorption model formulation).
For the Langmuir-advanced sorption model bi-dentate surface species are formed by complexation with two surface components (A and B).
For all sorption models except Freundlich and ion-exchange, Log(K_a) values of the surface species are adapted to log(K^c) values by ECOCALC using the correction for ionic strength (only for the dissolved component).
For the ion-exchange model surface species are automatically derived from the ion-exchange coefficients data for which a separate edit table has to be used (see chapter 2.1.8.4).
See chapter 2.1.9 for multiple run calculations for several variables (EDIT-MULTIPLE RUN-SURFACE SORPTION-SPECIES). See chapter 2.1.13 for optimization calculations with FIT + ECOSAT (EDIT-FIT).

2.1.8.4 Ion-Exchange coefficients

The Ion-Exchange coefficients for the particle surface with Gaines-Thomas ion-exchange as sorption model have to be defined in the ion-exchange coefficients edit table (select EDIT - ADSORPTION - SURFACE SORPTION - ION-EXCHANGE COEFFICIENTS).
Surface species are generated automatically after saving this edit table. Log(K_a) values are at that moment still incomplete formation constants: Log(K_a) values are adapted to log(K^c) values by ECOCALC using total particle amount (kg/l), total amount of the ion-exchange surface components (mol/kg) and the correction for ionic strength (only for the dissolved components).

2.1.8.5 Model parameters

Only for particle surfaces with a variable charge sorption model additional parameter values have to be specified in the model parameters edit table (go to EDIT - ADSORPTION - SURFACE SORPTION - MODEL PARAMETERS).
These parameter data can be added automatically from the database file if the database-auto-fill parameter has been set to *Yes* (default value). It is not possible to select them manually from the database file. Depending on the sorption model it concerns data like: specific surface area (m^2/kg), capacities, estimated potentials, sphere/cylinder radius, gel volume (also gel volume type and gel volume function parameters).
See chapter 2.1.9 for multiple run calculations for several variables (EDIT-MULTIPLE RUN-SURFACE SORPTION-PARAMETERS). See chapter 2.1.13 for optimization calculations with FIT + ECOSAT (EDIT-FIT).

2.1.9 Multiple run

Multiple run calculations (repeated runs) are set in the multiple run edit tables for the different possible variable groups: components, species, gases, minerals, organic liquids, particle surfaces, surface components, surface species and environment data (select EDIT - MULTIPLE RUN - …). There are two types of multiple run calculations possible:

A : The variable value is increased each time with a specific step value :

new value = (old value + step value) / (1 + volume change)

In this case specify the start value and the step value in the edit table for the relevant variable group. Select here also the multiple run dimension or calculation loop (1, 2, 3, 4 or 5) in which the automatic data change takes place. Total number of steps and volume change for each multiple run dimension are specified in the parameters edit table (EDIT - MULTIPLE RUN - DIM/FILE PARAM.).

B : The variable value for each step is read from data file *.MRF . (= multiple run file)

Multiple run calculations are possible for different data types and various units. Often also log values can be used (e.g. -log(activity)). Data types for which these multiple run calculations are possible :

Components	- Total amount (mol/l or mg/l), concentration (mol/l or mg/l), activity
	- Log(total amount), Log(concentration or activity), - Log(activity)
Species	- log(K^o)
Gases	- Partial gas pressure (bar, Pa, mol/l, or mg/l), Log(P-gas), Log(K_p)
Minerals	- log(K_{sol})
Organic liquids	- log(S_w), S_w
Particle surfaces	- Total amount (kg/l), initially adsorbed amount (mol/kg)
Surface components	- Total amount, site density (only vc-models), distribution parameters (only for heterogeneous models)
Surface species	- log(K_a), non-ideality parameter , Freundlich coefficients
	- Boltzmann factors for plane 0, 1 and 2
Model parameters	- Specific surface area, capacities, gel volume
Environment	- Ionic strength, temperature, gas volume and their log values

Up to 5 multiple run dimensions for the calculations of type A are available (5 nested loops). Besides that, all these data can be read from a data file (type B multiple run calculations). A constant volume change in case of for example a titration can also be specified. The default value for volume change equals zero. If data is read from file *.MRF no volume correction can be made.

Calculation order of the 6 multiple run loops (dimensions 1 till 5 and file data) :

$$\sum_{i}^{N_5}\sum_{j}^{N_4}\sum_{k}^{N_3}\sum_{l}^{N_2}\sum_{m}^{N_1}\sum_{n}^{N_{file}}(speciation)$$

with N_x = total number of runs in dimension x.

N_{file} : total number of data sets in file *.mrf.

The input data for multiple run calculations can also be read from data file *.MRF (Multiple Run File). In this file all data is listed in a special sequential order. This file can be made, with menu option EDIT - MULTIPLE RUN - READ MR FILE, using a spreadsheet file (e.g. *.PRN) as input. In this spreadsheet file all data has to be ordered in columns (only numeric data). This column ordered input data file can be made with a spreadsheet program, an (DOS) text editor, and also with the aid of menu option EDIT - MULTIPLE RUN - FILL MR FILE.

To make the *.MRF file :
Go to EDIT - MULTIPLE RUN - READ MR FILE - INPUT FILE and select the name of the input data file (e.g. with extension PRN). Then specify the total number of text lines (labels or blank) at the top of the file (option - TEXT LINES). Then specify in the edit table for column order (option - COLUMN ORDER) which data types can be found in the different columns. Select then option MAKE FILE to compose the *.MRF file (with the same name as the *.ECO file).

2.1.10 Cascade

In a cascade extraction calculation the total amount of components is adapted at each step by replacement of a certain volume of the water phase. To edit the extractant composition (added solution) select EDIT - CASCADE - EXTRACTANT COMPOSITION. To edit total number of cascade steps and replaced volume (default value = 1 liter/liter), select EDIT - CASCADE - PARAMETERS.

Cascade calculations are nested within the multiple run dimensions (loops) :

$$\sum_{i}^{N_5}\sum_{j}^{N_4}\sum_{k}^{N_3}\sum_{l}^{N_2}\sum_{m}^{N_1}\sum_{n}^{N_{file}}\sum_{p}^{N_{cas}}(speciation)$$

with N_{cas} = total number of cascade steps.

2.1.11 Reaction kinetics

See also appendix 2: Reaction kinetics in ECOSAT and appendix 4: Two-region and two-site kinetic model in ECOSAT.

Slow reaction kinetics or mass transfer include processes like :

- decay or decomposition
- adsorption or desorption
- precipitation or dissolution

Kinetic speciation calculations can be combined with multiple run, cascade and transport calculations. See chapter 2.1.13 for optimization calculations of slow mass transfer parameters with FIT + ECOSAT (EDIT-FIT).

Output parameters are the same as for transport (EDIT - KINETICS - PARAMETERS). For transport calculations it is not possible to edit here these parameters. Instead you have to edit them at TRANSPORT – PARAMETERS (see chapter 2.1.12.1).
In the rate equations edit table (EDIT - KINETICS - RATE EQUATIONS) differential equations for all time depending reacting components are formulated. These rate equation terms are of the form :

$$\sum_i b_i k_i \left(\prod_j c_{ij}^{x_{ij}} \right)$$

b : mass transfer coefficient; k = rate constant; c = species concentration; x = reaction order..

In each row of the edit table one term of this sum for component i has to be formulated.
See help files for detailed information.

Kinetic speciation calculations are nested within the multiple run dimensions (loops) and cascade calculations:

$$\sum_{i}^{N_5}\sum_{j}^{N_4}\sum_{k}^{N_3}\sum_{l}^{N_2}\sum_{m}^{N_1}\sum_{n}^{N_{file}}\sum_{p}^{N_{cas}}(kinetic\ speciation)$$

You have to formulate differential equations for **all components** which are affected by the slow mass transfer. Thus the slow reacting (surface) species or phase (mineral, organic liquid) has to be defined as a component. In case of transport these components, which are also present as **dissolved** species, are not always mobile. To disable mobility of species see § 2.1.12.4.

The partial differential equation is solved with a numerical integration method. Several choices for the integration method are possible: Euler-explicit method (Runge-Kutta order 2), Runge-Kutta order 4 with constant time step (more accurate), Runge-Kutta order 4 with variable time step (less accurate but

probably faster). The default setting is Euler-explicit. Time integration method can be set at menu option SETUP.

To see something happening on your screen during the kinetics speciation calculation, you can get time profiles of several variables in diagrams on your screen. At every time step this screen will be renewed. Several data types are possible. To realize this select EDIT - VIEW and edit the data in the view edit tables. Probably you will find it difficult to estimate the maximum values for the time profiles. Just try and look at the results in the diagrams or look at the output made with the output manager and adapt the maximum value for the next calculation.

2.1.12 Transport

In order to do transport calculations you have to define transport calculation type and all other transport data in the transport edit tables (EDIT - TRANSPORT - …). Transport of species in the gas phase or in the water phase are solved numerically for 1-dimensional or semi - 2- or 3-dimensional stationary flow.

To start a transport calculation:

- First build your system with components, species, gases, minerals, organic liquids, particle surfaces, surface components and surface species, environment parameter data, etc. (select EDIT - ...)

- Choose a transport calculation type: *(*select EDIT - TRANSPORT - PARAMETERS).
  Possible choices:

1D water flow	1-dimensional flow in the water phase
1D gas flow	1-dimensional flow in the gas phase
s2D water flow	semi 2-dimensional water flow
s2D gas flow	semi 2-dimensional gas flow
s3D water flow	semi 3-dimensional water flow
s3D gas flow	semi 3-dimensional gas flow

- Fill in all other transport parameter values (select EDIT - TRANSPORT - PARAMETERS).

- Define and edit soil column data sets (see figure 5): select EDIT - TRANSPORT - SOIL COLUMN.

- Define and edit feed data sets (see figure 6): select EDIT - TRANSPORT - FEED

- To see something happening on your screen during the transport calculation, you can get soil column data profiles in diagrams on your screen. At every time step this screen will be renewed. Several data types are possible. To realize this select EDIT - VIEW and edit the data in the view edit tables.

  Probably you will find it difficult to estimate the maximum values for the soil column profiles. Just try and look at the results in the diagrams or look at the output made with the output manager and adapt the maximum value for the next calculation.

- press F2 (save and go back to the ECOSAT main menu) and select RUN to start the calculation. Press space bar to break off transport calculations.

The transport equation is solved with a numerical integration method. Several choices for the integration method are possible: Euler-explicit method (Runge-Kutta order 2), Runge-Kutta order 4 with constant time step (more accurate), Runge-Kutta order 4 with variable time step (less accurate but probably faster). The default setting is Euler-explicit. Time integration method can be set at menu option SETUP.

See appendix 3 for information about the formulation of multicomponent transport
See appendix 4 for information about the two-site and the two-region kinetic transport-sorption models.
See appendix 5 for information about semi 2- and 3-dimensional flow

2.1.12.1 Transport parameters

Transport parameters like transport calculation type, soil column length, number of nodes, time step and time length, boundary condition, type of diffusion/dispersion coefficient, output for different time steps and nodes are set in the transport parameters edit table (EDIT - TRANSPORT - PARAMETERS).

Choose as transport calculation type:

1D water flow	:	1-dimensional flow in the water phase
1D gas flow	:	1-dimensional flow in the gas phase
s2D water flow	:	semi 2-dimensional water flow
s2D gas flow	:	semi 2-dimensional gas flow
s3D water flow	:	semi 3-dimensional water flow
s3D gas flow	:	semi 3-dimensional gas flow

For s2D and s3D flow you have to make a separate input file (*.s2D or *.s3D with * = ecosat file name). Go to INPUT s2D FILE or INPUT s3D FILE. See also § 2.1.12.7. and § 2.1.12.8.

For time step a suggestion is given based on two different stability criteria. One for dominant convective flow and one for dominant dispersive flow (see appendix 3).

Diffusion coefficients for species or gases and for suspended particles are set in this table. Dispersivity can be set in the soil column data sets (§ 2.1.12.2).

See appendix 3 for information about the 2 possible boundary conditions.

Select output for different time steps and nodes. Several options are available, like ALL, First, LAST, SEVERAL, SELECT, TIME or DEPT OUTPUT FILE (*.tof or *.dof). If you have a lot of specific output depths or moments you can use a data file (.tof or *.dof). This might be very convenient in case of optimizing transport parameters with FIT.

See chapter 2.1.13 for optimization calculations for the diffusion coefficient with FIT + ECOSAT (EDIT-FIT).

2.1.12.2 Soil Column

Soil column data is specified in the soil column edit tables. For each soil depth a soil column data set can be defined (figure 5). Each data set contains information concerning soil column composition and characteristics. The program creates always a default data set with the name *Basic: default*, in which component concentrations, particle surface amounts, gas pressures, environment data and soil column parameters are initially set to the (default) values in the corresponding edit tables (e.g. EDIT - COMPONENTS and EDIT - ADSORPTION - PARTICLE SURFACES).

First edit this default data set or define your own specific data set (select TRANSPORT - SOIL COLUMN - DEFINE or EDIT).

Use other soil column menu options to copy or delete specific soil column data sets or to get an overview of all data sets defined for certain soil column depths (option VIEW).
Initial soil column composition will be calculated with the data in the soil column edit tables:

- Component total amounts or concentrations are set in the soil column components edit table (select : TRANSPORT - SOIL COLUMN - EDIT - COMPONENTS). Also the constant calculation type can be set. Besides the types constant *'Total Amount', 'Concentration', 'Activity'* , *'P-gas -> Total amount'* and *'H2O -> Total amount'* 2 additional types are available: *'Concentration ->Total'* and *'Activity ->Total'*. They mean that for the first speciation calculation in each node for the whole soil column component **concentration** or **activity** is constant (=initial soil composition calculation), but that for all next calculations the **total amount** is constant and thus concentration or activity variable. Of course total amount will vary due to mass transport.

For transport calculations we normally don't use constant calculation types *'Concentration'* and *'Activity'* .

- Partial gas pressures are set in the gases edit table (select: TRANSPORT - SOIL COLUMN - EDIT - GASES).

- Total amount of particle surfaces is set in the soil column particle surfaces edit table (select: TRANSPORT - SOIL COLUMN - EDIT - PARTICLE SURFACES).

- Soil column parameters are set in the soil column parameters edit table (select TRANSPORT - SOIL COLUMN - EDIT - PARAMETERS). Here parameters like calculation type for ionic strength, ionic strength, temperature, volumetric water content, volumetric gas content and dispersivity for species and suspended particles are set. For s2D or s3D flow volumetric water content and volumetric gas content can also be set for each node in file *.s2d or *.s3d.

2.1.12.3 Feed

Feed data can be considered as input data for the upper boundary in the soil column. They are specified in the feed edit tables. For each time period a ***feed data set*** can be defined (figure 6). Each data set contains information concerning the feed composition and flow characteristics. The program creates always a default data set with the name *Start: default,* in which component concentrations, particle surface amounts, gas pressures and flow parameters are initially set to 0.0. Environment parameters (ionic strength and temperature) for the feed get the same (default) value as in the environment edit table (EDIT - ENVIRONMENT).

First edit this default data set or define your own specific data set (select TRANSPORT - FEED - DEFINE or EDIT).

Use other feed menu options to copy or delete specific feed data sets or to get an overview of all data sets defined for certain time periods (option VIEW).

Feed composition will be calculated with the data in the feed edit tables:

- Component data (total amount, concentrations, activities), have to be set in the feed components edit table (select TRANSPORT - FEED - EDIT (select data set) - COMPONENTS). Constant values can be given. However it is also possible to let ECOCALC calculate component total amount or concentration or activity as a function of time: select calculation type *Function* in stead of *Constant*. A linear or an exponential function can be chosen for each different component and their parameters can be set here.
  Also the constant calculation type can be set: constant *'Total Amount', 'Concentration', 'Activity'* , *'P-gas -> Total amount'* and *'H2O -> Total amount'.* For **gas** flow (constant partial gas pressure(s)) constant calculation data type for components in the gas phase will be *'P-gas -> Total amount".*
- Partial gas pressures are set in the gases edit table (select TRANSPORT - FEED - EDIT - GASES).
- Total amount of **suspended** particle surfaces is set in the feed particle surfaces edit table. Total amount of other particle types (solid and biota) is set to 0.0 (TRANSPORT - FEED - EDIT - PARTICLE SURFACES).
- Feed parameters are set in the feed parameters edit table (select TRANSPORT - FEED - EDIT - PARAMETERS). Here parameters like ionic strength calculation type, ionic strength, temperature and flux are set. For s2D or s3D flow flux for each node is read from file *.s2d or *.s3d.

2.1.12.4 Mobility

Sometimes it might be useful to exclude certain components, present in the form of dissolved species, from transport. In this edit table mobility of species in the water phase can be enabled. This can be a useful option in case of transport in combination with reaction kinetics (see § 2.1.11).

2.1.12.5 Read soil column file

Read column ordered data for components, gases, particle surfaces or environment parameters to fill soil column data sets. Go to EDIT - TRANSPORT - READ SOIL COLUMN FILE - INPUT FILE and select the input data file (e.g. with extension DAT or PRN). Then specify the total number of text lines (labels or blank) at the top of the file (option - TEXT LINES). Then specify in the edit table for column order (option - COLUMN ORDER) which data types (see chapter 3) can be found in the different columns. Select then option READ FILE to compose the soil column data sets.

2.1.12.6 Read feed file

Read column ordered data for components, gases, particle surfaces or environment parameters to fill feed data sets. Go to EDIT - TRANSPORT - READ FEED FILE - INPUT FILE and select the input data file (e.g. with extension DAT or PRN). Then specify the total number of text lines (labels or blank) at the top of the file (option - TEXT LINES). Then specify in the edit table for column order (option - COLUMN ORDER) which data types (see chapter 3) can be found in the different columns. Select then option READ FILE to compose the feed data sets.

2.1.12.7 Input s2D File

See also appendix 5: Semi-2D and semi-3D transport in ECOSAT.

Make *.s2D file for semi 2-dimensional transport. Go to EDIT - TRANSPORT - INPUT s2D FILE .
The file *.s2d (* = name of eco file) contains for **all nodes** the following data: flux (m/day), scale factor 1 (h1), scale factor 2 (h2), volumetric water content and volumetric gas content. Make this file with help of menu option INPUT s2D FILE - READ s2D FILE. The data will be read from a DOS-ASCII text file (e.g. *.prn) with the relevant data ordered in columns. Create this text file with help of menu option INPUT s2D FILE - FILL s2D FILE or with option INPUT s2D FILE - AXIAL SYMMETRIC or with any other DOS-text editor.
If you want to use the volumetric water and gas content as given in the soil column data sets, give negative values (e.g. -1) for these parameters in file *.s2d. Default values for the scale factors = 1.

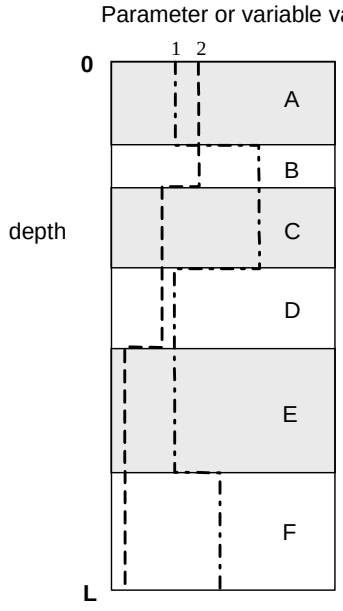
For axial symmetric cylindrical flow flux and scale factors 1 and 2 are calculated using input data for discharge (m^3/day), screen length and screen diameter (INPUT s2D FILE - AXIAL SYMMETRIC). For the volumetric water and gas content data in the soil column data sets is used. For that purpose negative values (-1) for water and gas content are given in file *.s2d.

2.1.12.8 Input s3D File

See also appendix 5: Semi-2D and semi-3D transport in ECOSAT.

Make *.s3D file for semi 3-dimensional transport. Go to EDIT - TRANSPORT - INPUT s3D FILE .
The file *.s3d (* = name of eco file) contains for **all nodes** the following data: flux (m/day), scale factor 1 (h1), scale factor 2 (h2), scale factor 3 (h3), volumetric water content and volumetric gas content. Make this file with help of menu option INPUT s3D FILE - READ s3D FILE. The data will be read from a DOS-ASCII text file (e.g. *.prn) with the relevant data ordered in columns. Create this text file with help of menu option INPUT s3D FILE - FILL s3D FILE or with option INPUT s3D FILE - RADIAL SYMMETRIC or with any other DOS-text editor.
If you want to use the volumetric water and gas content as given in the soil column data sets, give negative values (e.g. -1) for these parameters in file *.s3D Default values for the scale factors = 1.

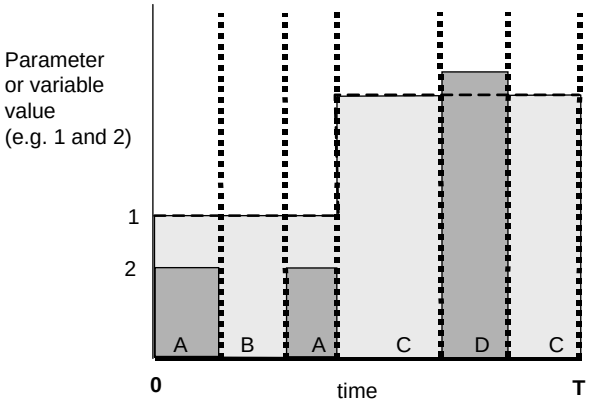
For radial symmetric spherical flow flux and scale factors 1, 2 and 3 are calculated using input data for discharge (m^3/day) and sphere diameter (INPUT s3dFILE - RADIAL SYMMETRIC). For the volumetric water and gas content data in the soil column data sets is used. For that purpose negative values (-1) for water and gas content are given in file *.s3d.



Soil column data sets :

- Set name (e.g. A)
- Depth
- Components total amount or concentration or activity
- Partial gas pressure
- Particle surface total amount
- Ionic strength
- Temperature
- Volumetric water content
- Volumetric gas content
- Dispersivity

Figure 5: Soil column data sets (A, B, C, D, E, F) for different soil depths. For example : dashed line component total amount and dashed-dotted line component activity (pH). Possible parameters and variables in the soil column data sets are indicated.



Feed data sets

Set name (e.g. A)
Time period
Component total amount or concentration or activity
Partial gas pressure
Particle total amount
Ionic strength
Temperature
Flux

Figure 6: Feed data sets (A, B, C, D) for different time periods. For example : solid line (dark gray) water flux and dashed line (light gray) component total amount. Possible parameters and variables in the feed data sets are indicated.

2.1.13 View

In case of transport calculations it is possible at runtime to look at calculated results for components, species, gases, minerals, organic liquids, particle surfaces, surface components, surface species, ionic strength and temperature for the soil column, in a diagram on the screen. Several data output types in default units are possible depending on the variable group : e.g. concentrations (mol/l), activities, total amounts (mol/l). This can be specified in the view edit tables (select EDIT - VIEW). There is a maximum of 10 diagrams possible.

See figure 7 and 8 for examples. Figure 7 shows the screen for a reaction kinetics calculation (see example file KIN_BT_1.eco) and figure 8 for a transport calculation (see example file TRA_CD_H.eco).

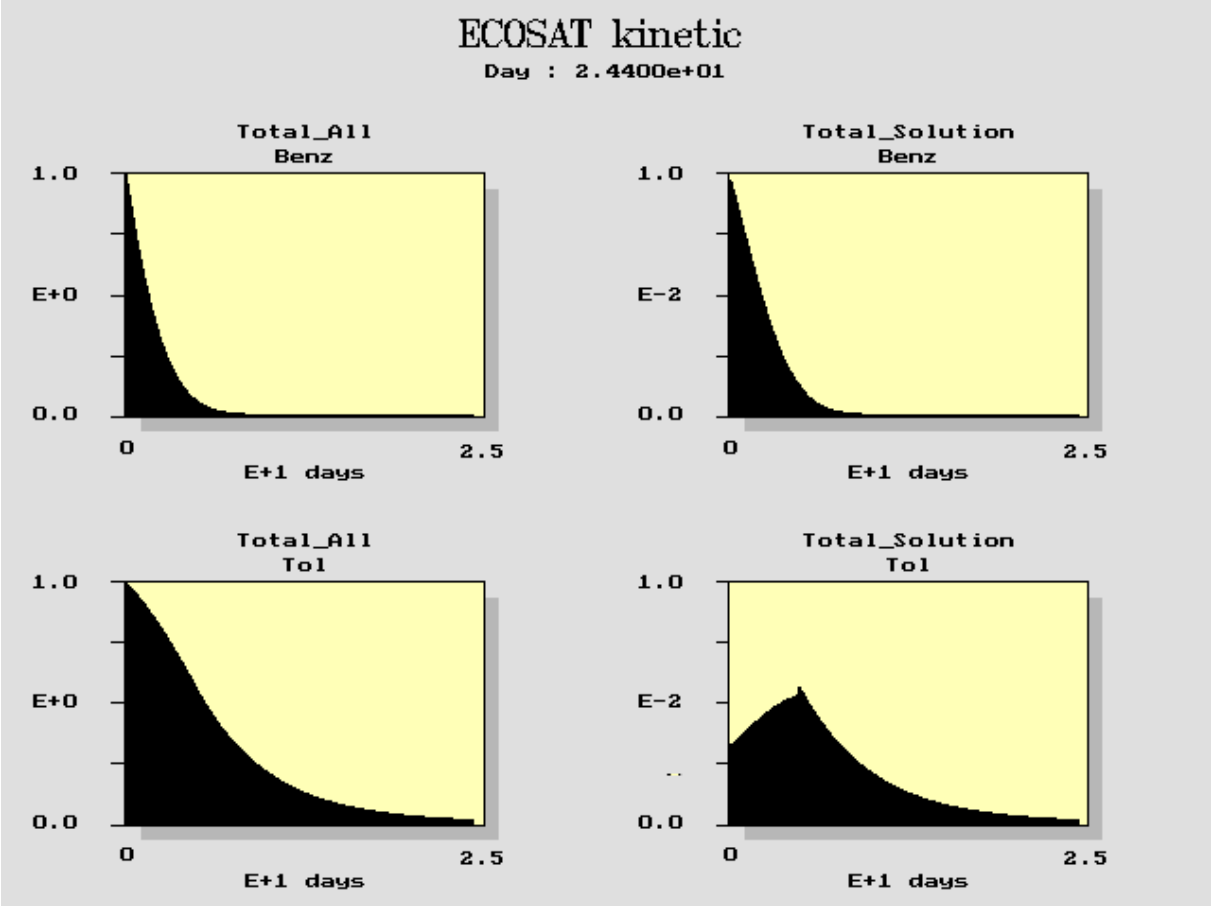


Figure 7 : Screen display of reaction kinetics calculation (example file KIN_BT_1.eco).
Different time curves in the diagrams; y-axis : variable value; x-axis : time (days).

Slow first order decay of a mixture of benzene and toluene in the water phase.

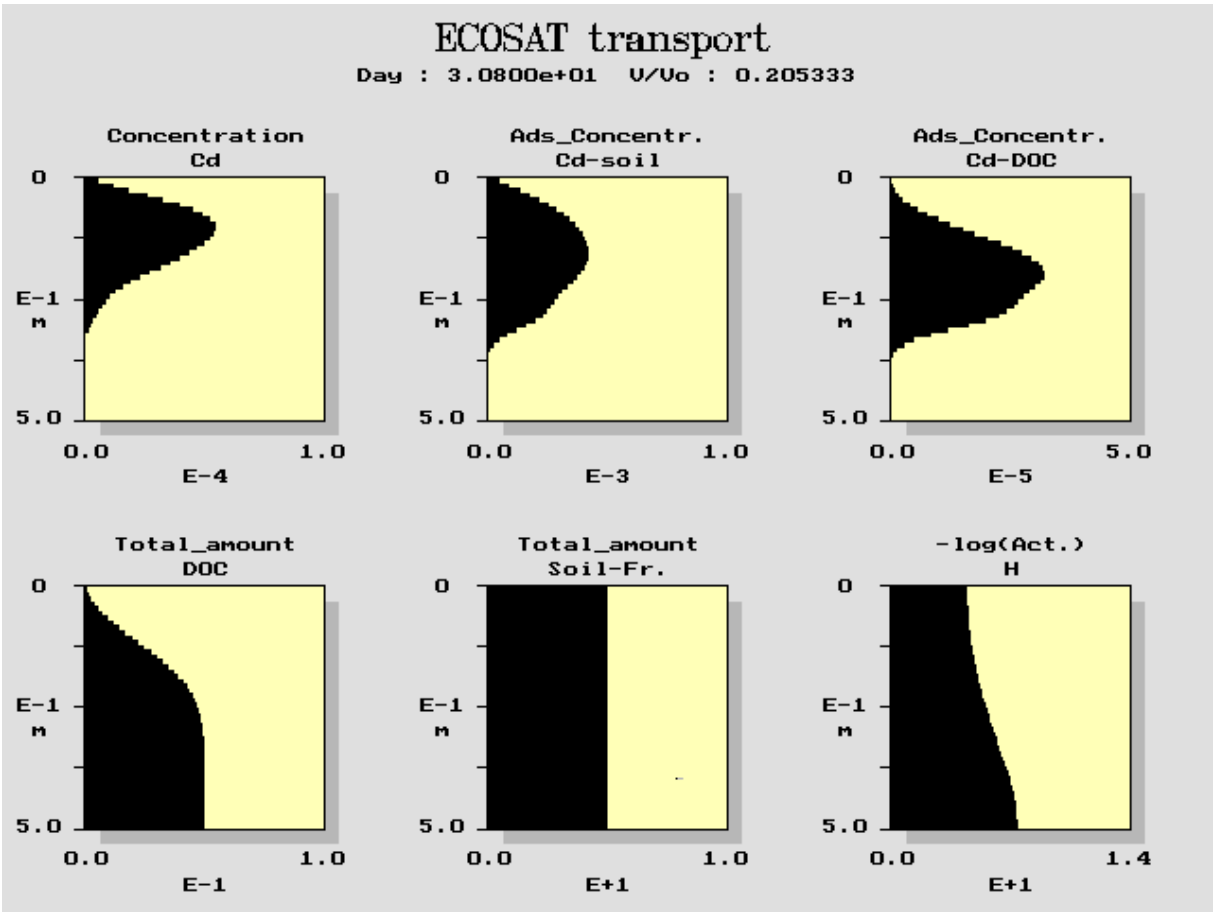


Figure 8 : Screen display of a transport calculation (example file TRA_CD_H.eco).
Different soil column concentration profiles in the diagrams.
y-axis : soil depth; x-axis : variable value.

Leaching of Cd due to deposition of acid rain; also leaching of DOC (dissolved organic carbon).

2.1.14 Fit

Here you can arrange input data in order to combine ECOSAT with the parameter fitting program FIT*. Parameter choice and all necessary input data for the dependent variable can be set.

* *Kinniburgh D.G. (1993): FIT User Guide, Technical Report WD/93/23, British Geological Survey, Keyworth.*

2.1.14.1 FIT + ECOSAT

ECOSAT will calculate the value's for the dependent variable (Y-calc) for a certain choice of parameters which have to be optimized. The FIT-program will adapt these parameters in an optimization process using known values for the dependent variable (Y-known) and ECOSAT will automatically start again to calculate new values for the dependent variable (Y-calc). This will be repeated until a predefined accuracy criterion in the FIT-program related to the difference between Y-known and Y-calc has been reached.

For parameter optimization several (more than 1) data points are required, for both Y-known and Y-calc. Therefore ECOSAT has to do a Multiple Run, a Cascade, a Kinetics or a Transport calculation. ECOSAT produces calculated values for the dependent variable (Y-calc). FIT compares these calculated values with the known values (Y-known) and adapts the parameter values. Y-calc values are saved in file outman.dat. Y-known values are stored in a file with any name and extension (e.g. *.dat with * = eco file name). Total number of Y-calc values has to be equal to total number of Y-known values.

ECOCALC will calculate speciation using the parameter values chosen in the FIT-edit tables and saved in file *.fit. FIT will adapt these parameter values in an optimization process based on Weighted Residual Sum of Squares (WRSS). File *.fit contains also other information for the FIT-program to start the whole optimization process. Results of the optimization process are saved in the FIT-program file *.res.

2.1.14.2 Data input

Both programs (FIT and ECOSAT) require their specific data input.
For FIT it is enough to (see also the help information in the FIT-program) :

- select ECOSAT (nr. ..) as model
- set the total number of parameters, their labels and their initial values
- set the total number of variables in the data input file (minimum of 2), and set which variable is the dependent one (Y-known).
- Set optimization parameters (e.g. convergence criterion, finite difference step size)

For ECOSAT the complete system for a speciation/transport calculation has to be formulated in an *.eco file. Extra data input has to be given in EDIT - FIT. Indicate which parameter has to be optimized (see EDIT-FIT- Parameter choices) and in which column of file outman.dat the calculated values (Y-calc) can be found (see EDIT-FIT- Dependent (Y) var).
It is possible to use available datasets for more than one variable (Y-known values). In that case you have to use option *Piled Columns* in the Output manager. The trick is that all Y-known values are placed on top of each other in one column. The Output manager will do that also for the calculated Y-values.

Possible parameter choices:

Components	:	Total amount
Species	:	Formation constant (log K^o)
Particle Surfaces	:	Total amount (kg/l)
	:	Initially adsorbed amount of a component (mol/kg)

Surface Sorption		
Surface Components	:	Total amount (mol/kg), Site density, heterogeneity parameter(s) (e.g. for)
Surface Species	:	log K_a, non-ideality parameter (e.g. for), Component coefficients (Freundlich exponents)
Surface parameters	:	Surface area, Capacity, Radius, Gel volume, Gel volume function parameters
Kinetics	:	Log K_r (rate constant). Reaction order coefficient
Transport	:	Transport parameters (e.g. Diffusion coefficient or Dispersivity)

2.1.14.3 Procedure

Procedure for parameter optimization with FIT using ECOSAT as model (see figure 9).

1 Create ecosat file (*.eco) with Multiple Run, Cascade, Kinetics or Transport calculation. Use a first estimate of the parameters to be optimized. Be sure that the calculated values for the dependent variable (Y-calc) correspond with the known (measured) values (Y-known).

2 Save or Run ECOSAT (it creates FIT_ECO.bat, FITEXEC.bat and *.fit)
Run ECOSAT to check the calculation and to select output.

3 Select output, at least Y-calc, with the output manager (OM).
Be sure that total number of Y-calc values equals total number of Y-known values. Selected output is automatically saved in outmanin.sof.

4 Start ECOSAT input manager again and edit Fit data (EDIT - FIT).
- Select parameters to be optimized (- PARAMETER CHOICE)
- Insert column position of Y-calc in file outman.dat (-DEPENDENT (Y) VAR.) and save (replace file) or run again.

5 Start FIT with FITECO (here we assume that FIT is located in subdirectory **C:/FIT**) and define parameter optimization problem (create file *.def):
- Choose ECOSAT as model.
- Insert input data file (*.dat) with the Y-known values and set the position (column) of the dependent variable.
- Insert initial values for the parameters.
- Insert output file name for the optimization results.

6 Run FIT; FIT automatically starts ECOCALC, reads Y-calc from outman.dat, adapts parameter values which will be saved in *.fit, and restarts ECOCALC again. ECOCALC reads the parameter data in *.fit and of course all system data from file *.eco. Parameter data in *.fit overrules parameter data in *.eco.
The ECOSAT output manager starts automatically with arguments M and F (OUTMAN M F) forcing OUTMAN to generate output automatically conforming the selected output stored in outmanin.sof (argument M) and prevents output to the screen (argument F).

7 View results of the parameter optimization in the FIT output file (*.res).

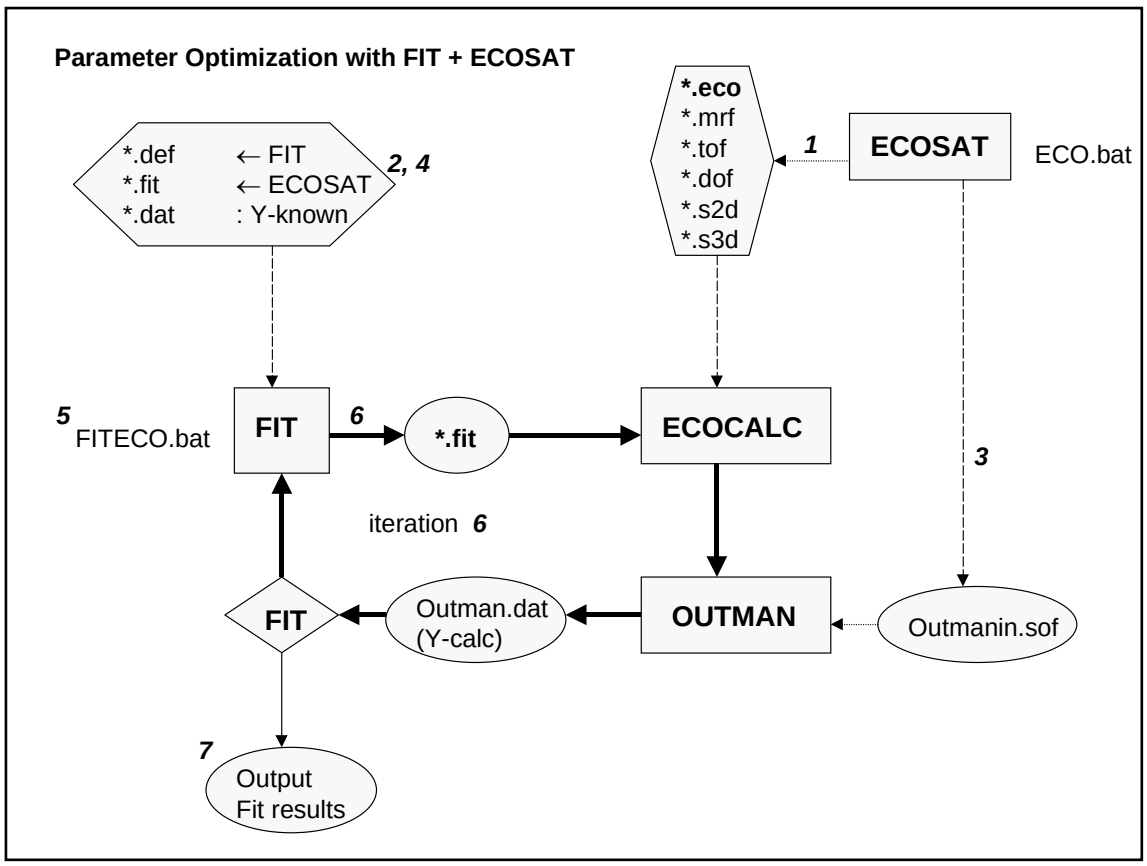


Figure 9: Parameter optimization with FIT and ECOSAT: processes (see text for explanation of the indicated ***numbers***), programs and files.

2.2 Database files

The database files contain data for the variable groups : components, species, gases, minerals, organic liquids, particle surfaces, surface components, surface species and chemicals. These data files are user expandable (select DBASE - DBASE GROUP).
The database files always have a default extension (.db*). For every variable group a different third extension character is used.
Except for components you can create for all variable groups your own database files.
Maximum capacity for the database files : 200 items (rows).

ECOSAT standard default database files :

Components	: ECOCOMP.dbA
Species	: ECOSPEC1.dbB
Gases	: ECOGAS.dbC
Minerals	: ECOMIN1.dbD
Organic liquids	: ECO_ORG.dbE
Particle surfaces	: ECOPART.dbP
Surface sorption data	: ECOPART.dbS
Chemicals	: ECO_CHEM.dbG

Available standard ECOSAT database files for species and minerals :

ECOSPEC1.dbB :	all species not present in the other species database files.
ECOSPEC2.dbB :	all Ag, Hg, Ni, SiO_4, SeO_4, Se, AsO_4, Br, I, F and $B(OH)_4$ species.
ECOCHELA.dbB :	all EGTA, DTPA, HEDTA, CDTA, EDTA, NTA species.
ECOCYAN .dbB :	all CN and $Fe(CN)_6$ species.
ECOACIDS.dbB :	all Acetate (Ac), Oxalate (Ox) and Citrate (Cit) species. all amino acids.
ECO_ACTI.dbB :	all U and UO species (actinides)
ECOMIN1.dbD :	all minerals not present in ECOMIN2 or ECOMIN3.
ECOMIN2.dbD :	all SiO_4, MoO_4, SeO_4, Ag, Se, As and Hg minerals.
ECOMIN3.dbD :	all U and UO_2 minerals.

The ECOPART.dbS database for surface sorption data contains examples of data for different types of sorption models for particle surfaces mentioned in file ECOPART.dbP. Included is some recent data for NICA-sorption of heavy metals on humic acid and sorption data of metals and oxy-anions on HFO (Hydrous Ferric Oxide).

Data from database files for a specific variable group can be selected in the corresponding edit table (go to the first column and press ENTER; choose **Select from Dbase** in the displayed window).
Automatic addition of (surface) species, gases, minerals or organic liquids for newly added (surface) components or particle surfaces from the database files is possible if the auto fill parameters for the relevant variable groups are enabled.

Building your own speciation system starts with selection of components from the components database file (ECOCOMP). After saving the components edit table the program will automatically search for other relevant variables (e.g. species, gases, minerals, organic liquids) in the available database files. When found they will be added to the edit tables. However this automatic procedure is not recommended for gases and minerals.
You can switch off this automatic '**search and add'** procedure by disabling the auto fill parameter for the specific variable group (go to DBASE - DBASE GROUP - AUTO FILL).

2.3 Build

Via menu option BUILD, you can create a new system using total amounts of chemicals, minerals or organic liquids as input. ECOSAT will automatically generate the components, species, etc. belonging to that system. It is also possible to **add** total amounts of chemicals, minerals or organic liquids to an existing system.

Specify the data in the build-edit tables (select BUILD - CHEMICALS or - MINERALS or -ORG.LIQUIDS). Select then - BUILD SYSTEM and make a new system or add the data to the existing system.

Check always the results of this procedure (select menu option EDIT - ...) !

2.4 Tools

At menu option TOOLS, you can find several extra facilities:

- Calculation of $\log(K^c)$ or $\log(K^o)$ at a specific ionic strength for dissolved species, gases or minerals (select TOOLS - K^o <---> K^c). The data in this edit table can be added to the selected database file.

- In the edit tables (NOT in the database files) automatic replacement of a component by a dissolved species or gas (select TOOLS - REPLACE COMPONENT).

Check always the results of this procedure !

2.4 File

At menu option FILE several options to handle the *.ECO files can be found : Retrieve, Save, Delete, choose a new file, etc. With option NEW FILE all edit tables (*.TMP files) are cleared and you can start with a complete new system. With option BATCH you can do several different ECOSAT runs after each other. The *.ECO files are put in a batch file.

2.5 PC and program setup

PC and program setup parameters can be adjusted in the edit table SETUP.
These program parameters determine the maximum number of iteration steps and convergence criteria for various numerical procedures. Time integration method can be chosen and the B-parameter in the Davies-equation can be set (see also ENVIRONMENT - ionic strength).
Factors for estimating transport time step (F1 and F2) are set here.
For multiple run calculations a parameter can be set in order to use the previous calculated component results as estimates for the next calculation.

All these default values are saved in file ecosat48.ini which is a copy of eco_sat.ini. Ecosat48.ini is only active for the (sub)directory in which it resides. To change eco_sat.ini and thus all future ecosat48.ini files, choose option *'save permanently'.*

3 Output manager

Start the program with: **OM** (DOS) or click button ***ECOSAT: output*** in ECOSHELL (Windows).

The output manager OUTMAN can only be used for output selection of calculated data saved by ECOCALC in the *.ECO files. The input manager ECOSAT **only** writes the system description to *.ECO files (input for ECOCALC). Calculated output data saved by ECOCALC in these files can be used as input for the output manager OUTMAN.

With the output manager you can select and compose specific output. Output is saved in file OUTMAN.DAT which can be read by a spreadsheet program or text editor. The output selections are saved in a data file with extension SOF (Selections Output File). Default name : OUTMANIN.SOF (see also figure 1).

The introduction screen of OUTMAN is very similar to that of ECOSAT. The same function keys are available. In stead of the menu options EDIT and RUN, OUTMAN has the menu options CHOICE and MAKE (see figure 10).

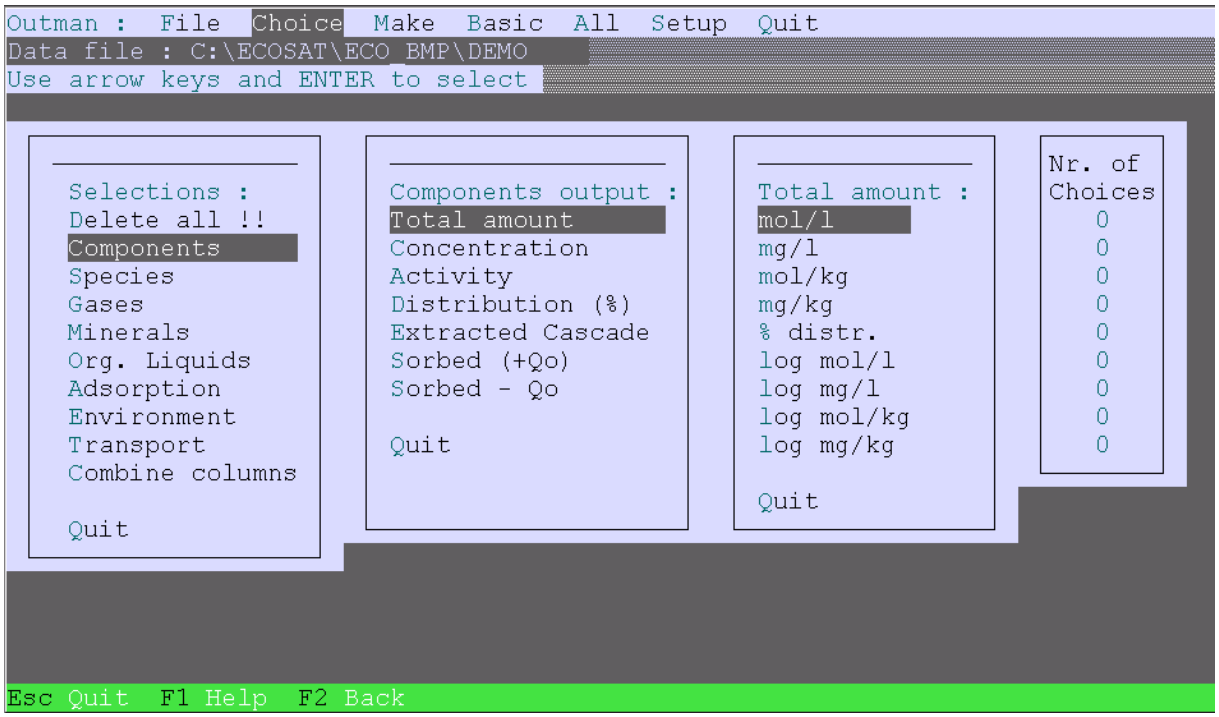


Figure 10. Components output choice menus in the output manager (selection order : Choice > Components > Sorbed > mol/kg)

Output manager main menu options:

File — Select data file (*.ECO) or selections output file (*.SOF). The program uses default OUTMANIN.SOF as selections input file.

Choice — Selection of output for components, (dissolved) species, gases, minerals, organic liquids, particle surfaces, surface components, surface species, environment parameters, transport data (concentration profile or breakthrough curve), combine columns and pile (stack) columns.

Make — Make selected output and write data into file OUTMAN.DAT; save output selections in file OUTMANIN.SOF.

Basic — Write basic output to file OUTMAN.DAT (basic output = output from ECOCALC, saved in file *.ECO). This is the minimum output needed for OUTMAN to calculate all other output.

All — Write basic output + all species concentrations to file OUTMAN.DAT.

Setup — PC set up.

Quit — Make file OUTMANIN.SOF and quit program (no output).

In stead of *edit tables* OUTMAN works with so called *choice tables* where different types of output for specific variables can be chosen from a menu displayed in a window (figure 11).

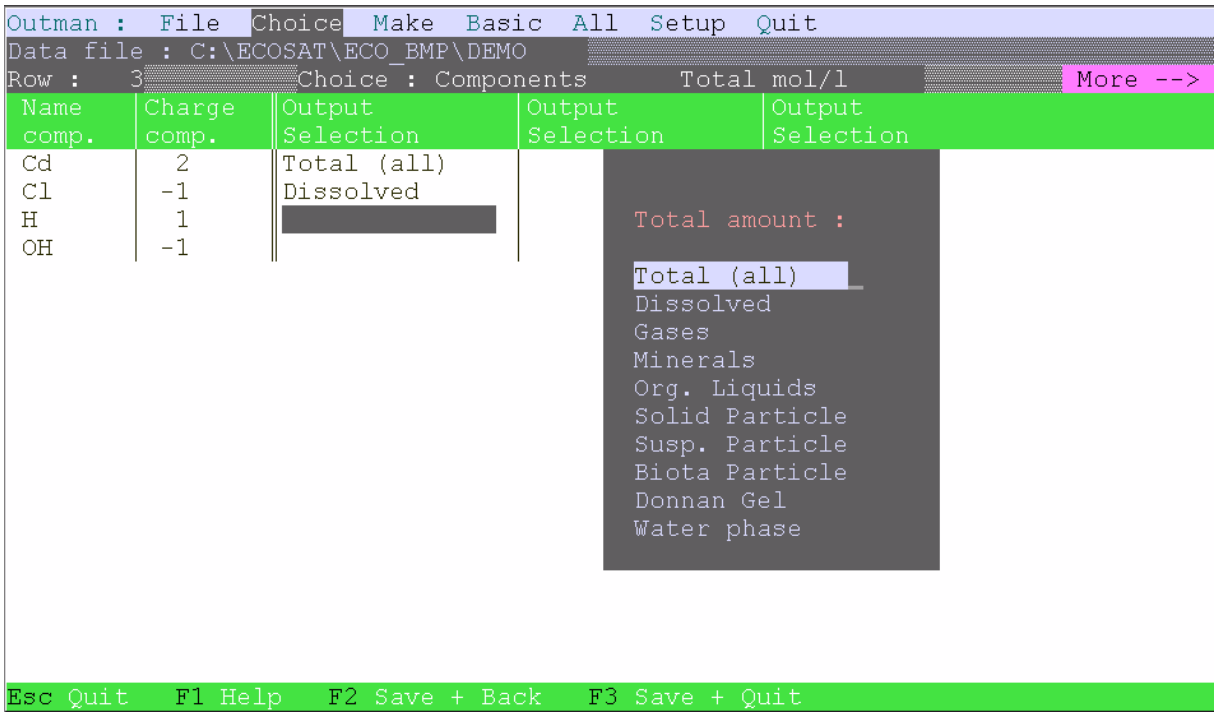


Figure 11. Components output choice menu in the output manager

OUTMAN uses the data in the edit tables of the input manager as input for the system description or creates these edit tables first on retrieving the selected *.ECO file. For each variable group (component, species, gas, mineral, organic liquid, particle surface, surface component, surface species, environment parameters) you can select different types of output in these choice tables (select CHOICE). Delete all former choices with option *Delete all*.

After output selection you can select MAKE to create the selected output. OUTMAN reads then the calculated output data of ECOCALC in file *.ECO, calculates the selected output and writes the results to file OUTMAN.DAT. The output selection itself, is stored in the default file OUTMANIN.SOF.

Data in OUTMAN.DAT is presented in columns for each output item (not for option BASIC). The first rows are reserved for labels. Other rows contain calculated data for each step in the multiple run or cascade calculations and for each output moment or depth in the transport calculation and for each output moment in the kinetics speciation calculation.

For transport two different output formats are possible:
- soil column profile data for specific time steps (see also figure 9)
- breakthrough concentration curve data for specific nodes
  (select CHOICE - TRANSPORT - XY FORMAT).

Appendix 1

Speciation calculations in ECOSAT

Speciation calculations in ECOSAT

Speciation

Speciation deals with the chemical equilibrium distribution of compounds over different forms and phases in the soil-water system. All distribution reactions are formulated in terms of reacting components and distribution constants. For all components mass balance equations are formulated and solved numerically with a Newton-Raphson algorithm. Possible different types of species are : dissolved species in the water phase (ion pairs, complexes, free components), gases, minerals, organic liquids ((D)NAPL), surface species (adsorbed components onto soil particles). Ionic strength and temperature corrections are made with the Davies equation and the Van 't Hoff equation.
The standard approach followed in solving chemical equilibria is based on formulation of the mass balances for all components and expressing the species concentrations in terms of component concentrations and formation constants. An overview of all relevant equations can be given in a so called table of species. For a system with only the components A and B and the species A_nB_m this is shown in table 1.

Table 1 : Table of species

Components	A	B	log(K)
Species (mol/l)			
A	1	0	0
B	0	1	0
A_nB_m	n	m	$\log(K_{AnBm})$
Total amount (mol/l)	A(t)	B(t)	

Reading this table in vertical direction gives an expression for the mass balances of the components. For example $A(t) = [A] + n[A_nB_m]$. In horizontal direction the expression for the species concentration is given. For example $[A_nB_m] = [A]^n[B]^m.K_{AnBm}$.
For all types of species and phases present in the system this approach is followed as much as possible. Only in some specific cases special adaptations in the solution procedure have been made. Some topics related to speciation calculations are discussed here in more detail. For more information see the textbooks on Chemical equilibria in soil, water, sediment; part B and on Chemical sorption in the soil-water system.

Minerals mixture

If a mineral is present in a system the solubility reaction is used as an extra equation leading to reduction of the number of independent mass balances. As long as the mineral is present, its total mineral amount is not important for the equilibrium solution because mineral activity equals 1.
For the case of equilibrium with a mixture of minerals special care has been taken in ECOSAT to ensure that all possible combinations of minerals are evaluated. A special algorithm has been developed to find as fast as possible the correct mineral composition of the system.
The decision which minerals are present at equilibrium is based on comparison of ion activity products with solubility constants and on comparing calculated total amounts of components compared with the known total amounts.

Organic liquid mixture (DNAPL or NAPL mixture)

If a mixture of pure organic liquids is present the distribution calculation becomes much more complicated due to the fact that the total amount of the components present in the mixture influences the concentration of the components in the water and gas phase (Raoult's law). This makes a different approach necessary from the normal solution scheme as used for minerals where total mineral amount is not important at all. For example for a mixture of benzene and toluene the mass balances for the components benzene and toluene may be formulated as :

Benz(t) = [Benz(L)] + [Benz(aq)] + [Benz(g)] + [Benz(ads)]
Tol(t) = [Tol(L)] + [Tol(aq)] + Tol(g)] + [Tol(ads)]

(L) : pure organic liquid form; (aq) : dissolved in water; (g) : gas form;
(ads) : adsorbed onto soil particle surfaces.

The concentrations in the different phases (water, gas, adsorbed) can be expressed in terms of the total amount of the pure organic liquid. In case of linear adsorption knowledge of the K_d is sufficient for describing sorption behaviour. Further information about water solubility (S) and Henri's constant (H) is needed.

Assume [Benz(L)] = x and [Tol(L)] = y; where x/(x+y) equals the mol fraction of benzene and y/(x+y) the molfraction of toluene in the mixture:

$Benz(t) = x + x/(x+y) * S_{Benz} + x/(x+y) * S_{Benz} * H_{Benz} + x/(x+y) * S_{Benz} * K_{d,Benz}$
$Tol(t) = y + y/(x+y) * S_{Tol} + y/(x+y) * S_{Tol} * H_{Tol} + y/(x+y) * S_{Tol} * H_{Tol} * K_{d,tol}$

S : water solubility; H : Henry constant; K_d : soil/water distribution constant

These equations can be solved according to the standard procedure by taking x and y as components. Derivatives for the elements of the Jacobian matrix in the Newton-Raphson iteration method are determined numerically. The decision on the presence of the organic liquid is based on comparison of the concentrations in the water phase with the water solubility (S). This might give some numerical inaccuracy !

In table 2 an example of the table of species for a system containing benzene and toluene is shown. If total amounts of benzene and toluene are high enough to exceed water solubility a mixture of both aromatic compounds will be present and Raoult's law ($C_w = n.S$; n = mole fraction) has to be used to calculate speciation assuming ideal behaviour of the compounds benzene and toluene. This is formulated in table 3.

Table 2. Table of species for benzene + toluene (no mixture present).

Components	**Benzene**	**Toluene**	**log K**
Species (mol/l)			
Benz(w)	1	0	0
Tol(w)	0	1	0
Benz(g)	1	0	$\log(H_{g,Benz})$
Tol(g)	0	1	$\log(H_{g,Tol})$
Q_{benz}	1	0	$\log(K_{d,Benz})$
Q_{tol}		1	$\log(K_{d,Tol})$
Phases			
Benz(L)	1	0	S_{Benz}
Tol(L)	0	1	S_{tol}
Total amount (mol/l)	Benz(t)	Tol(t)	

For a mixture of both organic liquids: introduce new components and adapt log K for all relevant species.

Table 3. Table of species for benzene + toluene; mixture of organic liquids present.

Components	**Benz(L)**	**Tol(L)**	**log K***
Species (mol/l)			
Benz(w)	1	0	$\log(S_{benz})$
Tol(w)	0	1	$\log(S_{Tol})$
Benz(g)	1	0	$\log(S_{Tol}) + \log(H_{g,Benz})$
Tol(g)	0	1	$\log(S_{Tol}) + \log(H_{g,Tol})$
Q_{benz}	1	0	$\log(S_{benz}) + \log(K_{d,Benz})$
Q_{tol}		1	$\log(S_{Tol}) + \log(K_{d,Tol})$
Benz(L)	1	0	0
Tol(L)	0	1	0
Total amount (mol/l)	Benz(t)	Tol(t)	

* Calculate species concentrations by dividing log K with [Benz(L)] + [Tol(L)]

ECOSAT adapts automatically the table of species in case of the presence of organic liquid mixtures.

Sorption models

To describe adsorption or desorption different types of sorption models are available in ECOSAT. Components adsorb to particle surfaces where surface sites (surface components) react with the component resulting in bound components (= surface species). Taking electrostatic effects into account leads to the so called variable charge (VC) models. Possible VC models are : Diffuse Double Layer (DDL), Basic Stern (BS), Constant Capacitance (CC), Triple layer and Donnan. The surface complexation reactions are described with the Langmuir equation or with heterogeneous sorption models.
For more simplistic approaches non variable charge (NVC) models can be applied : Freundlich (including linear sorption), Langmuir and Gaines-Thomas for ion exchange.
A specific VC-model is the Surface Precipitation Model (SPM) of Farley, Dzombak and Morel (in Dzombak and Morel, 1990).

For both VC and NVC sorption models also heterogeneity of the particle surface can be taken into account using specific surface site complexation models in stead of the standard Langmuir equation. Possible heterogeneous sorption models are : NICA, CONICA, Langmuir-Freundlich, Generalized Freundlich and Toth.

It is possible in ECOSAT to relate the total amount of the particle surface to the calculated total amount of a specific mineral. Total amount of the mineral (mol/l) is converted then into kg/l using the molar mass of the mineral. This might be interesting for e.g. oxides.

Sorption of suspended particles like DOC (Dissolved Organic Carbon) is important in modelling transport and bio-availability of organic chemicals (PHA, pesticides) and heavy metals. At this moment ECOSAT can calculate transport of suspended particles but exclusive particle interactions. Interaction of (suspended) particles with the soil matrix is a recent research topic and will be implemented in a later version.

The standard approach in solving chemical equilibria is followed as much as possible. Often extra specific components are introduced and log(K) values adapted. Mass balance formulations are changed sometimes and derivatives of the mass balance functions are determined analytically or numerically.
Some of the possible sorption models are discussed here in more detail. For more information see the textbook on Chemical sorption in the soil-water system.

Freundlich
Heavy metal behaviour in soils is quite often reasonably well described with the empirical multi component Freundlich model. For example for cadmium sorption interaction of pH, zinc and calcium has been reported, leading to formulations like :

$Q_{Cd} = K_{Cd}.(Cd)^a.(H)^b.(Zn)^c.(Ca)^d$ with Q_{Cd} in mol/kg.

According to the standard speciation calculation the dimension of the surface species Q_{Cd} has to be changed into mol/l. This makes adaptation of the log(K) value necessary : K^*_{CD} = .K_{Cd} with = soil solution ratio in kg/l.

The multicomponent Freundlich equation is not an expression for competitive sorption but includes only several interaction terms. The most important one is the pH dependency of heavy metal sorption. However in standard speciation programs this formulation should lead to wrong expressions for the mass balances of all components involved (e.g. ***a*** mol Cd or ***c*** mol Zn per mol Q_{Cd}). To solve this problem parameter values are changed in the calculation of the mass balances : ***a*** gets the value 1 in the mass balance for Cd and ***b***, ***c*** and ***d*** get the value 0 in the mass balances for H, Zn and Ca respectively. An example of this approach is presented in table 34with sorption of components A and B according to :

$Q_A = K^F_A.(A)^n(B)^m.$ $Q_B = K^F_B.(B)^p$

Table 4 : Table of species for Freundlich sorption of components A and B

Components	**A**	**B**	**log(K)**
Species (mol/l)			
A	1	0	0
B	0	1	0
$\mathbf{Q_A}$	n,1	m,0	$\log(K^F_A) + \log \rho$
$\mathbf{Q_B}$	0	p,1	$\log(K^F_B) + \log \rho$
Total amount (mol/l)	**A(t)**	**B(t)**	

Sorption of organic chemicals can often be described with the most simple form of the Freundlich model : $Q = K^F.C^n$ with n = 1 (linear adsorption model) and $K^F = K_d = F_{OM}.K_{om}$ (K_d = distribution constant).
f_{OM} = fraction organic matter and K_{OM} = organic matter/water distribution constant. In ECOSAT $\log(K_{OM})$ can be used if $\rho.f_{OM}$ is taken for the total amount of the soil particle surface present in the system.

Langmuir
The Langmuir model describes sorption of components on the soil particle surface according to the surface complexation reaction : S + A $\leftrightarrow$ SA. Competition between components for the same surface sites is included in the formulation of the model (multicomponent Langmuir) :

$$\theta_i = \frac{K_i C_i}{1 + \sum_{i=1}^{n} K_i C_i}$$

C_i : concentration of component i
K_i : sorption affinity constant for component i
$_i$: fraction of sites occupied by the adsorbed component i
for component A : $_A$ = [SA]/S(t), with S(t) = total number of sites.

The Langmuir model is easily incorporated in the standard formulation as the distribution constant K_i is dimensionless. Calculations can be based on fractions ( ) or total amounts (mol/l). For the Langmuir Advanced model (bidentate sorption) K_i has to be expressed in terms of θ_i, because otherwise it should not be dimensionless.

In table 5 the table of species is given for competitive sorption of components A and B. S(t) is the total number of sites available for sorption (mol/l). S(t) = $\rho.Q_{max}$ with Q_{max} equal to the total number of sorption sites in mol/kg.

Table 5 : Table of species for Langmuir sorption of components A and B

Components	**S**	**A**	**B**	**log(K)**
Species (mol/l)				
A	0	1	0	0
B	0	0	1	0
S	1	0	0	0
SA	1	1	0	$\log(K^L_A)$
SB	1	0	1	$\log(K^L_B)$
Total amount (mol/l)	**S(t)**	**A(t)**	**B(t)**	

Ion exchange

Ion exchange is calculated according to Gaines-Thomas (GT). The exchange coefficient is defined as :

$$K_{GT(X_nA \rightarrow X_mB)} \equiv \frac{(E_B)^{1/m}(A)^{1/n}}{(E_A)^{1/n}(B)^{1/m}}$$

based on the exchange reactions:

Gaines-Thomas: $1/n\ X_nA + 1/m\ B^{m+} \leftrightarrow 1/m\ X_mB + 1/n\ A^{n+}$

E = sorbed equivalent fraction

For the Gaines-Thomas ion exchange model implementation in a standard speciation program is not straightforward. This is due to the different dimensions used for the sorbed amount : dimensionless in the exchange model versus mol/l in the speciation model. It implies recalculation of the value of the exchange coefficient into a value for the formation constant of the surface species. The free surface site can be considered as an extra component of which the total amount is equal to the cation exchange capacity (CEC in mol p^+/kg). This surface component will not be present in the form of a species as all sites are occupied by cations (This in contrast to the Langmuir model).
Reformulating the exchange reaction into surface complexation reactions, taking one of them as the reference reaction with log(K) = 0, results in adapted log(K) values for all other ion exchange reactions (see table 6).

$$K_B = \left(\frac{n^{1/n}\,[X(t)]^{1/m}}{m^{1/m}\,[X(t)]^{1/n}} K_{GT} \right)$$ and X(t) = ρ.CEC (mol/l) with ρ in kg/l

Using the exchange coefficients for ion pairs the relevant surface reactions with their log K values are formulated automatically by the input manager of the ECOSAT program.

Table 6 : Table of species for Gaines-Thomas ion-exchange of components A and B.

Components	**X**	**A**	**B**	**log K**
Species (mol/l)				
A	0	1	0	0
B	0	0	1	0
$\mathbf{X_nA}$	n	1	0	$n \log(K_{reff}) = 0$
$\mathbf{X_mB}$	m	0	1	$m \log K_B$
Total amount (mol/l)	**X(t)**	**A(t)**	**B(t)**	

Heterogeneous models

Sorption of heavy metals onto organic matter is often only satisfactorily described if heterogeneity of the organic matter surface, caused by different reactivity of reaction sites, is taken into account. Different models have been implemented in ECCOSAT. The most important ones are :

Langmuir-Freundlich : $$\theta_i = \frac{\tilde{K}_i C_i}{\sum_i \tilde{K}_i C_i} \cdot \frac{(\sum_i \tilde{K}_i C_i)^m}{1 + (\sum_i \tilde{K}_i C_i)^m}$$

with m = heterogeneity parameter which characterizes the width of the $\log(K_i)$ distribution function. i ranges from 1 to the total number of all competing components. $\tilde{K}_i$ = median affinity constant of component i for the surface site.

NICA (non ideal competitive adsorption) :

$$\theta_i = \frac{(\tilde{K}_i C_i)^{n_i}}{\sum_i (\tilde{K}_i C_i)^{n_i}} \cdot \frac{(\sum_i (\tilde{K}_i C_i)^{n_i})^p}{1 + (\sum_i (\tilde{K}_i C_i)^{n_i})^p}$$

n_i and p are model parameters indicating ion specific and surface site specific heterogeneity interactions respectively.

NICA (non ideal competitive adsorption; Kinniburgh, 1999):

$$\theta_i = \frac{n_i}{n_H} \cdot \frac{(\tilde{K}_i C_i)^{n_i}}{\sum_i (\tilde{K}_i C_i)^{n_i}} \cdot \frac{(\sum_i (\tilde{K}_i C_i)^{n_i})^p}{1 + (\sum_i (\tilde{K}_i C_i)^{n_i})^p}$$

To follow the standard calculation procedure surface components are introduced to express the formulation of the surface species concentration in terms of the components and the median affinity constant. It is not necessary to take the surface components also as surface species because the free surface sites are not included in the formulations of the heterogeneous models.

Variable charge models

Sorption of anions and cations onto organic matter or metal (hydr)oxides is often well described taking electrostatic effects into account. In ECOSAT the charging behaviour can be described with well known models like Diffuse Double Layer (DDL), Constant Capacitance (CC), Basic Stern, Triple Layer and Donnan. Due to the presence of a charged field counter ions are accumulated in a double layer near the particle surface. The surface complexation reaction can be described with the Langmuir model or with one of the heterogeneous models using the local component concentration in stead of the equilibrium bulk concentration. The local component concentration and the equilibrium concentration in the bulk solution are related via the electrostatic potential at the surface ($_o$) according to the Boltzmann equation.

For example for component A :

$$[A^z]_s = [A^z]\ e^{-zF\psi_o/RT} = [A^z]\ B_o$$

B_o = Boltzmann factor for the surface layer.
F : Faraday constant (= 96491 C/mol p^+); T : temperature (K); R : gas constant (= 8.31 $J.mol^{-1}K^{-1}$).

Depending on the chosen VC-model other extra layers plus Boltzmann factors are defined (B_1 for DDL, BS, Triple layer, Donnan and B_2 for Triple layer). These Boltzmann factors are introduced as extra (electrostatic) components making calculation of species concentration possible according to the standard procedure. The total amount of this electrostatic component equals to the change of charge due to sorption in the surface layer. Charge and potential are related via the chosen VC-model. An example of the formulation of VC-sorption is given in table 7.

Table 7: Table of species for sorption of component A according to the Langmuir-DDL model.

Components	**B_o**	**S**	**A**	**log(K)**
Species (mol/l)				
A	0	0	1	0
S	0	1	0	0
SA	1	1	1	$\log(K_A)$
Total amount (mol/l)	**$\rho(\ _o - z_c F N_s)/F$**	**$S(t) = \rho.N_s$**	**A(t)**	

S(t) = total number of sites on the particle surface (mol/l);
N_s = total number of sites (mol/kg); ρ = soil solution ratio (kg/l).
$_o$ = surface charge; z_c = charge of the surface component (= -1);
F = Faraday constant.

The charge calculated using the mass balance equation is compared with the charge calculated on basis of the electrostatic model. In the ECOSAT model it is not necessary to take integer charges for the surface groups (z_c) on the soil particle surface(s). In ECOSAT it is at this moment not possible to calculate the composition of the DDL !

For sorption of metals on organic matter the NICA-Donnan is very appropriate. In the Donnan model the potential in the Donnan volume or gel volume (B_1) and the concentrations of the dissolved species are equal for the whole volume (homogeneous system). Given a certain gel volume it is rather easy to calculate the composition of the gel volume (see table 8).
The gel volume often depends on ionic strength. In ECOSAT it is possible to calculate gel volume als function of (variable) ionic strength during runtime. This function is a log linear relation for which both parameters (a, b) can be adapted for each particle surface:

$\log V_d = a + b.\log I$ with I : ionic strength (mol/l)
V_d : gel volume (l/kg)
a, b : parameters

Table 8. Table of species for a system with sorption according to the NICA-Donnan model.

Components	$\mathbf{B_o}$	**S**	**A**	**B**	**log K**
Species (mol/l)					
A	0	0	1	0	$\log K_A = 0$
B	0	0	0	1	$\log K_B = 0$
$\mathbf{A_2B}$	0	0	2	1	$\log K_{A2B}$
Gel species					
A	z_A	0	1	0	$\log(\rho.V_d) + \log K_A$
B	z_B	0	0	1	$\log(\rho.V_d) + \log K_B$
$\mathbf{A_2B}$	z_{A2B}	0	2	1	$\log(\rho.V_d) + \log K_{A2B}$
Surface species					
SA	a_{SA}	1	1	0	$\log K_{a,SA}$
SB	a_{SB}	1	0	1	$\log K_{a,SB}$
Total amount (mol/l)	$\mathbf{z(t)=-\rho.F.N_s\sum a_i}$	$\mathbf{S(t) = \rho.N_s}$	**A(t)**	**B(t)**	

z_i : ion valence; a_i : change of charge due to formation of the surface species relative to the charge of the free surface site (S);
z(t) : change of charge due to sorption; $z(t) = -\rho.F.N_s\sum a_i$ with i = SA or SB.
S(t) = total number of sites on the particle surface (mol/l);
N_s = total number of sites (mol/kg); ρ = soil solution ratio (kg/l).
F = Faraday constant;

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Appendix 2

Reaction Kinetics

in

ECOSAT

Reaction kinetics in ECOSAT

Slow mass transfer reactions taking place in soil-water systems like decay of organic compounds, desorption from organic matter and dissolution of minerals are described according to the next general formulation :

Mass transfer reaction: aA + bB $\leftrightarrow$ cC + dD

A is a component and B, C and D are species. a, b, c and d are stoichiometric coefficients.

Rate equation for component A: $$\frac{d[A]}{dt} = -\mathrm{K}_1[A]^{\mathrm{x}}[B]^{\mathrm{y}} + \mathrm{K}_2[C]^{\mathrm{p}}[D]^{\mathrm{q}}$$

K_1 is the forward rate constant (mol/(l.day)); K_2 the backward rate constant. x, y, p and q are parameters related to the reaction order of A with respect to the species B, C and D.

If B, C and D are components, rate equations have to be formulated for these components as well. For example for component C:

$$\frac{d[C]}{dt} = +\frac{\mathrm{c}.}{\mathrm{a}}\mathrm{K}_1[A]^{\mathrm{x}}[B]^{\mathrm{y}} - \frac{\mathrm{c}}{\mathrm{a}}\mathrm{K}_2[C]^{\mathrm{p}}[D]^{\mathrm{q}}$$

The partial differential equation is solved numerically using an integration method. Several choices for the integration method are possible: Euler-explicit method (Runge-Kutta order 2), Runge-Kutta order 4 with constant time step (more accurate), Runge-Kutta order 4 with variable time step (less accurate but probably faster). The default setting is Euler-explicit. Time integration method can be set at menu option SETUP.

Examples of slow mass transfer reactions:

- Decay of compound A: A + x O_2 $\leftrightarrow$ CO_2 + H_2O

  Assume O_2-dependend first order decay of component A: $$\frac{dA_{total}}{dt} = -\mathrm{K}_{\mathrm{r}}[A]^1[O_2]^{\mathrm{n}}$$

  with [A] the concentration of A in the water phase.
  A_{total} equals the total amount of A in the system (mol/l).

  For O_2: $$\frac{d[O_2]}{dt} = -\mathrm{x}.\mathrm{K}_{\mathrm{r}}[A]^1[O_2]^{\mathrm{n}}$$
  with $[O_2]$ the O_2-concentration in the water phase.
  x = transfer coefficient (number of moles O_2 used per mol A).

- Slow desorption of component A (see also appendix 4)

  The driving force for adsorption or desorption is the difference between the actually adsorbed amount and the adsorbed amount at equilibrium.

  SA $\leftrightarrow$ S + A K_a (soil/water distribution constant)

  $$\frac{d[SA]}{dt} = -\mathrm{K}_1[SA]^{\mathrm{x}} + \mathrm{K}_2[A]^{\mathrm{p}}[S]^{\mathrm{q}} = -\mathrm{K}_1\left([SA]^{\mathrm{x}} - \mathrm{K}_{\mathrm{a}}[S]^{\mathrm{p}}[S]^{\mathrm{q}}\right)$$

The driving force for slow mass transfer is the difference between the really adsorbed amount ([SA]) and what it should be at equilibrium (often x = p = q = 1).

- Slow dissolution of the mineral A_aB_b

  $A_aB_b \leftrightarrow aA + bB$ K_s (solubility constant)

  Here the driving force is not the difference between actual total mineral amount and total mineral amount at equilibrium which will have minor influence on the dissolution rate, but for instance the difference between ion activity product (IAP) and the solubility constant (K_s) for that mineral. At equilibrium K_s = IAP. Of course this a rough approximation of the real process.

$$\frac{d[A_aB_b]}{dt} = -K_1.K_s\left(1-\frac{IAP}{K_s}\right)$$

and for example for component A: $$\frac{d[A]}{dt} = -a.K_1.K_s\left(1-\frac{IAP}{K_s}\right)$$

Appendix 3

Multicomponent transport in ECOSAT

Multicomponent transport in ECOSAT

In ECOSAT transport is limited to 1-dimensional stationary water or gas flow. 2- or 3-dimensional water or gas flow however can be simulated as if it is 1-dimensional using mathematical transformations. This is called semi 2-dimensional or semi 3-dimensional flow (see appendix 3). Gas flow is treated in the same way as water flow: no local pressure influence on the gas flow and the gas is assumed to be incompressible. ECOSAT needs input of the water or gas flux for the whole calculation period and for the whole soil column (= all nodes).

The 1-dimensional convection diffusion/dispersion equation used is formulated as:

$$\frac{\partial C_{i,total}}{\partial t} = D \frac{\partial^2 C_{i,\text{mobile}}}{\partial x^2} - v \frac{\partial C_{i,mobile}}{\partial x}$$

$C_{i,mobile}$: total amount of component i in the mobile phase (water or gas).
$C_{i,total}$: total amount of component i in the system ($C_{i,mobile}$ + $C_{i,imobile}$).
D : diffusion/dispersion coefficient in the mobile phase (same value for all species); $D = D_{diffusion} + D_{dispersion} = D_{diff} + D_L .v$ with D_L = longitudinal dispersivity (m).
v : pore velocity of the mobile phase ($v = v_D/\theta$ with v_D the Darcy flux and θ the volumetric water or gas content).
x, t : distance and time.

For gas flow only gases and for water flow all dissolved species and components bound to suspended particles (suspended surface species) are taken as the mobile species. Suspended particles are thus also transported. The partial differential equation has to be solved for all components affected by transport and all suspended particles.

The 1-dimensional convection diffusion/dispersion equation is solved numerically with the method of finite differences using the stream-upwind scheme for the advection term and central differences for the dispersion/diffusion term. This is only possible if boundary conditions are given. In ECOSAT 2 different formulations of the boundary conditions can be chosen:

Boundary Condition 1 (BC1): $C_{i,mobile}(0,t) = f(t)$ (= feed concentration)

$$\frac{\partial C_{i,mobile}(L,t)}{\partial x} = 0$$

with x = distance; t = time; L=column length; $C_{i,mobile}$ = mobile total amount of component i and f = feed composition at time t (in node 0).

Boundary Condition 2 (BC2):

$$V_D.C_{i,mobile}(0,t) - \theta.D\frac{\partial C_{i,mobile}(0,t)}{\partial x} = J_0(t) = V_D.C_{i,mobile}(0,t)$$

$$\frac{\partial C_{i,mobile}(L,t)}{\partial x} = 0$$

with x = distance; t = time; L= column length; $C_{i,mobile}$ = mobile total amount of component i; f = feed composition at time t (in node 0); θ = volumetric water or gas content; v_D = Darcy flux; D = diffusion/dispersion coefficient; J_0 = flux at node 0.

BC1 is the default boundary condition applicable for most situations (e.g. soil column leaching studies). BC2 can be used in situations where at node 0 no mass transfer by diffusion/dispersion is possible (e.g. impermeable layer).

Due to the numerical solution method (finite differences) one should take care of proper choices for the numerical grid. These choices depend on the values for the flux (v_D) and the diffusion/dispersion coefficient (D). Which of these two variables is the most important can be estimated with the column Peclet number (Pe*):

$$Pe^* = \frac{V_D.L}{\theta.D}$$ column Peclet number; L = column length

For Pe* > 100 convection dominates and for Pe* <100 diffusion becomes important. For large Pe* stable solutions are found, at least for mono component transport if $\beta_{mix} < 1$:

$$\beta_{mix} = \frac{v.\Delta t}{R.\Delta x} < 1$$

R = retardation factor: $R = 1 + \frac{\rho \partial Q}{\theta \partial C}$

with Q the adsorbed amount (mg/kg), C the concentration in the water phase (mg/l), ρ the dry bulk density (kg/l) and θ the volumetric water content.

For small Pe* values stable solutions are found for $\alpha_{mix} < ½$, at least for mono component transport:

$$\alpha_{mix} = \frac{D.\Delta t}{R.\Delta x^2} < ½$$

For multicomponent transport more **strict** stability criteria are often necessary (e.g. $\alpha < 1/3$), partly because R varies then often with time. Too small time steps increase numerical dispersion caused by to many calculations each with numerical truncation errors. Sharp concentration fronts will always become diffuse due to numerical dispersion. Take Δt as large as possible for a certain choice of Δx. To increase accuracy smaller Δx values, and thus also smaller Δt values (stability criterion), can be taken.

Combination of for example slow sorption with transport leads to the following formulation of the 1-dimensional convection diffusion/dispersion equation :

$$\frac{\partial C_{i,T}}{\partial t} = D \frac{\partial^2 C_{i,\text{mobile}}}{\partial x^2} - v \frac{\partial C_{i,\text{mobile}}}{\partial x}$$

with $C_{i,T}$: total amount of component i in the whole system (mol/l or mg/l) (= f(speciation)).
$C_{i,mobile}$: total amount of the component in the mobile phase (mol/l or mg/l).

See appendix 4 for more information about the well known 2-site and 2-region models to describe slow mass transfer of components in soil column leaching studies.

To solve the multicomponent transport equation next steps are followed:

at t = 0 : Determine $C_{i,T}$ in all nodes of the numerical grid (boundary condition for t = 0 and x > 0*).* Determine $C_{i,mobile}$ by speciation calculation.

at t = t + Δt : Calculate $C_{i,T}$ in all nodes using the transport equation.
Determine $C_{i,mobile}$ by speciation calculation.
Determine $C_{i,mobile}$ for node 0 (= feed composition) This equals the boundary condition for x = 0 and t > 0.

Speciation and mass transport are thus calculated independently.

Appendix 4

Two-region and two-site kinetic models in ECOSAT

Two region and two site kinetic models in ECOSAT

Two-region kinetic model

The two-region kinetic model of Parker and Van Genuchten (1984) conceptually divides the porous medium into two domains. Due to the heterogeneous pore size distribution, pore water can be more or less mobile. Parker and Van Genuchten assume that the pore water is either mobile or immobile (stagnant). Further they assume that diffusion in the immobile region is negligible.
Because species in the mobile region are not in (local) equilibrium with species in the immobile region, we have to double the species table. In table 1.1 this extended species table for the simple system that is described in Gaber et al. (1995) is shown. In this system we have only one component, which can be present in both regions in dissolved and adsorbed form. Although elaborated here for a mono component system it can be applied to a multicomponent system as well.
As adsorption model a linear Freundlich model is used: $Q_C_i = K_dC_i$. This is not a restriction, the two-region approach can be used in combination with **any other** adsorption model.

Table 1.1 Table of species belonging to a simple two-region kinetic model

components	C_m	C_{im}	log(K)
species			
C_m	1		0
C_{im}		1	0
$Q^*_C_m$	1		0.15
$Q^{**}_C_{im}$		1	0.15
total amount C_T (mol/l)	0.1	0.1	

To indicate in which region the species and components are present, we have given them an index *m* or *im* for the mobile and immobile region respectively. Sorption of the component C_m on particle surface Q* in the mobile region and of C_{im} onto particle surface Q** in the immobile region. In each separate region the dissolved species (C_m or C_{im}) is in chemical equilibrium with the adsorbed species ($Q^*_C_m$ or $Q^{**}_C_{im}$). Mass transfer from one region to the other is assumed to be proportional with the difference in concentration of the dissolved species (C_m-C_{im}). $C_{m,T}$, C_m and $Q^*_C_m$ are expressed in mol/l mobile water and $C_{im,T}$, C_{im} and $Q^{**}_C_{im}$ in mol/l immobile water. Schematically this system is presented in figure 1.1.

In figure 1.1 the solid arrows between two species indicate that they are in equilibrium. The dotted arrows indicate that mass transfer is rate limited.

The slow mass transfer equation can be formulated as: $$\frac{\partial S_{im,T}}{\partial t} = \alpha\left(C_m - C_{im}\right) \quad (1)$$

with $S_{im,T}$ the total amount of the component in the immobile region (dissolved and adsorbed):

$$S_{im,T} = \theta_{im}C_{im} + (1-f)\rho K_dC_{im} \text{ mol/l soil} \quad (2)$$

with *f* the mobile water fraction: $\theta_m = f.\theta$ and $\theta_{im} = (1-f)\theta$ the immobile water fraction.
ρ is the soil bulk density (kg/l) and K_d the distribution constant (l/kg).
α is the mass transfer rate constant (d^{-1}).
C_m in mol/l mobile water and C_{im} in mol/l immobile water.

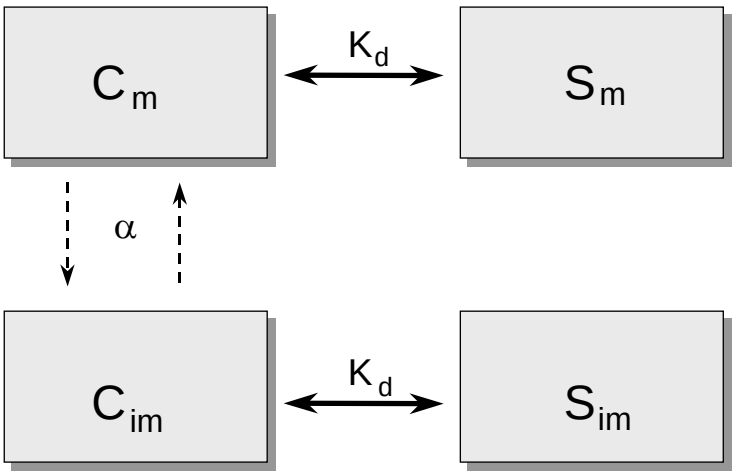


Figure 1.1. Schematic representation of the concept upon which the two-region model is based (linear sorption model).

The governing transport equations to describe the 2-region system mathematically are:

$$\frac{\partial C_{m,T}}{\partial t} = \left(1 + \frac{f\rho \mathrm{K_d}}{\theta_m}\right)\frac{\partial C_m}{\partial t} = L(C_m) - \frac{\partial S_{im,T}}{\theta_m \partial t} \tag{3}$$

$$L(C_m) = -v\frac{\partial C_m}{\partial x} + \mathrm{D_m}\frac{\partial^2 C_m}{\partial x^2} \tag{4}$$

$$\frac{\partial S_{im,T}}{\partial t} = (\theta_{im} + (1-f)\rho \mathrm{K_d})\frac{\partial C_{im}}{\partial t} = \alpha(C_m - C_{im}) \tag{5}$$

v : local pore velocity (m/d)
D_m : diffusion/dispersion constant for the mobile water region (m^2/d).

In the mobile region transport of solutes is described by an advective-dispersion equation. In the immobile region it is assumed that there are no advective, diffusive and dispersive fluxes. Furthermore it is assumed that the rate of solute exchange between the mobile and immobile region can be described by a first order process with mass transfer constant α.

We will now rewrite equation 3 and 5 in a formulation that can be used by ECOSAT. First we will substitute equation 5 into equation 3. We then get:

$$\frac{\partial C_{m,T}}{\partial t} = \left(1 + \frac{\rho^{*} \mathrm{K_d}}{\theta_m}\right)\frac{\partial C_m}{\partial t} = L(C_m) - \frac{\alpha}{\theta_m} C_m + \frac{\alpha}{\theta_m} C_{im} \tag{6}$$

with $\rho^* = f.\rho$

Dividing equation (5) with θ_{im} gives:

$$\frac{\partial C_{im,T}}{\partial t} = \frac{\partial S_{im,T}}{\theta_{im}\partial t} = (1_{im} + \frac{\rho^{**} \mathrm{K_d}}{\theta_{im}})\frac{\partial C_{im}}{\partial t} = \frac{\alpha}{\theta_{im}} C_m - \frac{\alpha}{\theta_{im}} C_{im} \tag{7}$$

with $\rho^{**} = (1-f)\rho$

Substitution with $k_1 = \frac{\alpha}{\theta_m}$ and $k_2 = \frac{\alpha}{\theta_{im}}$ results into

$$\frac{\partial C_{m,T}}{\partial t} = L(C_m) - \mathrm{k_1} C_m + \mathrm{k_1} C_{im} \tag{8}$$

$$\frac{\partial C_{im,T}}{\partial t} = \mathrm{k_2} C_m - \mathrm{k_2} C_{im} \tag{9}$$

$C_{m,T}$ and $C_{im,T}$ are the total amounts of the component C in the mobile and immobile region respectively.

Note that C_m is expressed in mol/l mobile water and C_{im} in mol/l immobile water. Although not really necessary we can convert C_{im} into the more convenient unit mol/l mobile water, using

$$C'_{im} = \frac{\theta_{im}}{\theta_m} C_{im} \quad \text{with } C'_{im} \text{ in mol/l mobile water} \tag{10}$$

and rewrite equations (8) and (9):

$$\frac{\partial C_{m,T}}{\partial t} = L(C_m) - \frac{\alpha}{\theta_m} C_m + \frac{\alpha}{\theta_{im}} C'_{im} = L(C_m) - \mathrm{k_1} C_m + \mathrm{k_2} C'_{im} \tag{11}$$

$$\frac{\partial C'_{im,T}}{\partial t} = \frac{\alpha}{\theta_m} C_m - \frac{\alpha}{\theta_{im}} C'_{im} = \mathrm{k_1} C_m - \mathrm{k_2} C'_{im} \tag{12}$$

Now we have to fill in the speciation and transport data into ECOSAT. The data we will use are summarized in tables 1.1. and 1.2. Take $\theta = \theta_m$ and $D = D_m$.

Table 1.2 Speciation and transport data for the two-region model

Soil column data	
ρ (soil bulk density) kg/l soil	1.5
θ_m (volumetric mobile water content)	0.2
θ_{im} (volumetric immobile water content)	0.3
L (column length) m	1
$C_{m,T}$ (initial total amount) mol/l mobile water	0.1
$C_{im,T}$ (initial total amount) mol/l immobile water	0.1
Sorption data	
f (fraction of sites in mobile region)	0.4
log K_{Fr} (Freundlich equilibrium constant)	0.15
n (Freundlich exponent)	1
α (mass transfer constant) d^{-1}	1.5
Transport data	1.0
v_D (Darcy flux) m/d	1.0
D (diffusion/dispersion coefficient) m^2/d	0.005
Feed concentration in mol/l mobile water	0

We choose here to express C_{im} in mol/l mobile water (= C'_{im}); see also example TWO_REG2. See example TWO_REG1 for C_{im} in mol/l immobile water.
Initially the system is in a state of chemical equilibrium.

Using the input manager of ECOSAT we have to fill in several input tables. In the following the most relevant input tables are shown.

First we discuss the input for C_{im} in mol/l immobile water (file TWO_REG1). In file TWO_REG2 C_{im} is expressed in mol/l mobile water. The latter is more convenient e.g. because total amounts in both regions can be added then without any correction in order to calculate total amount adsorbed.
See screen dumps on the next pages (the files can be found in directory .\ECOSAT\EXAMPLES).

Components edit table :

Ecosat : File Build Edit Run Dbase Tools Setup Quit
File : C:\ECOSAT\EXAMPLES\TWO_REG2
Row : 4 ; Edit : Components More -->

Name comp.	Charge comp.	Constant Calc. Data type	Total amount (mol/l)	(Estimated) log(Conc./Act.)	Molar mass (g/mol)
C_m	0	Total amount	1.0000000E-01	-1.000000	1.0000
C_im	0	Total amount	1.5000000E-01	-1.000000	1.0000

In the first column both components in the mobile and immobile region, C_m and C_{im}, are defined. The total amount of $C_{m,T}$ is 0.1 mol / l mobile water and for $C_{im,T}$ 0.15 mol/l immobile water. The value for $C'_{im,T}$ = 0.1 x 0.3/0.2 = 0.15 mol/l mobile water.

Species edit table :

Ecosat : File Build Edit Run Dbase Tools Setup Quit
File : C:\ECOSAT\EXAMPLES\TWO_REG2
Row : 4 ; Edit : Species More -->

Name species	log(Ko) (298.15 K)	delta H kJ/mol	Molar mass **********	Reference comment	Coeff.
C_im	0.0000	0.0000	0.0000		1.0000
C_m	0.0000	0.0000	0.0000		1.0000

Species edit table continued:

Ecosat : File Build Edit Run Dbase Tools Setup Quit
File : C:\ECOSAT\EXAMPLES\TWO_REG2
Row : 4 ; Edit : Species More -->

delta H kJ/mol	Molar mass **********	Reference comment	Coeff.	Comp.	Coeff.	Comp.
0.0000	0.0000		1.0000	C_im		
0.0000	0.0000		1.0000	C_m		

We have here only the 2 dissolved species C_m and C_{im}. Mind that species C_{im} is not mobile !

Particle surfaces edit table:

Adsorption : Particle surfaces Surface sorption Qo Interactions Quit
File : C:\ECOSAT\EXAMPLES\TWO_REG2
Row : 4 ; Edit : Particle surfaces More -->

Particle Surface	Particle Type	Related Mineral	Total amount (kg/l)	Sorption model	Geometry **********
Q*	Solid		3.0000E+00	Freundlich	-
Q**	Solid		3.0000E+00	Freundlich	-

We have defined two particle surfaces. Q* is the particle surface in the mobile region and Q** is the particle surface in the immobile region. The total amount we have to fill in is the soil solution ratio. So, here Q* = $f\rho/\theta_m$ = 0.4 x 1.5/0.2 = 3.0 kg / l mobile water and Q** = $(1-f)\rho/\theta_{iim}$= 0.6 x 1.5/0.3 = 3 kg/l immobile water.

Freundlich surface species edit tables :

We have to fill in two **Freundlich surface species tables** because we have defined two particle surfaces (Q* and Q**). For both surface species Q*_C_m and C**_C_im log K_{Fr} = 0.15.

Adsorption : Particle surfaces Surface sorption Qo Interactions Quit
Particle surface : Q*
Row : 3 ; Edit : Freundlich surface species More -->

Surface species	log(K-Fr) (at T)	Reference comment	Coeff.	Sorbed Comp.	Coeff.	Comp.
Q*_Cm	0.1500		1.0000	C_m		

Surface sorption edit table for particle surface Q*
Surface species Q*_C_m with log K_{Fr} = 0.15

Adsorption : Particle surfaces Surface sorption Qo Interactions Quit
Particle surface : Q**
Row : 3 ; Edit : Freundlich surface species More -->

Surface species	log(K-Fr) (at T)	Reference comment	Coeff.	Sorbed Comp.	Coeff.	Comp.
Q**_Cim	0.1500		1.0000	C_im		

Surface sorption edit table for particle surface Q**
Surface species Q**_C_im with log K_{Fr} = 0.15

Kinetics - rate-equations edit table:

Now we have to define the kinetic part of the transport equation. From the menu we choose the option **Kinetics – rate equation**. In this table we define the terms of the kinetic part of the transport equations. These terms look like

$$\sum_i b_i k_i \left(\prod_j c_{ij}^{x_{ij}}\right) \qquad (13)$$

In each row of this table we can define one term of this sum. The constant b_i is the transfer coefficient and can have the value of +/- 1. The constant k_i is the rate constant at 298.15 K. Values of this constant at other temperatures can be calculated using the Arrhenius constant according to:

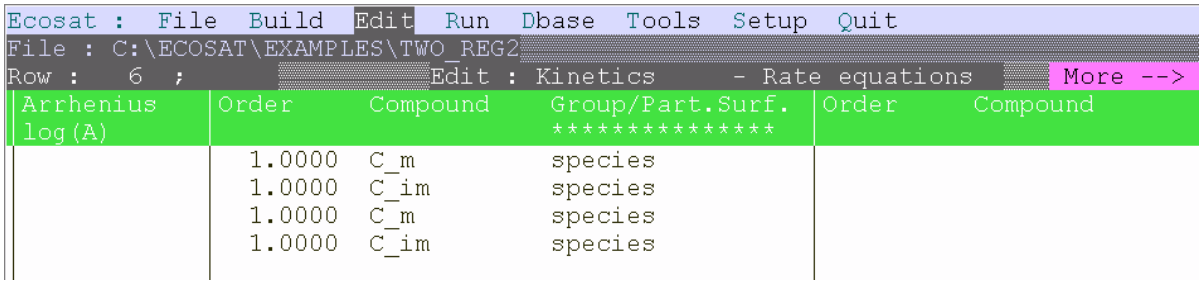
$$\ln(k_i) = -Ea / RT + \ln(a) \qquad \text{(see ECOSAT help)} \qquad (14)$$

The constant x_{ij} is the order of the reaction with respect to the compound C_{ij}. We can choose as compounds any of the species in the system. In this case the dissolved species C_m and C_{im}.

Ecosat : File Build Edit Run Dbase Tools Setup Quit
File : C:\ECOSAT\EXAMPLES\TWO_REG2
Row : 6 ; Edit : Kinetics - Rate equations More -->

dC/dt or +	Comp. (C)	Transfer Coeff.	Rate const. log(Kr)	Arrhenius -Ea/R	Arrhenius log(A)	Order
dC/dt	C_m	-1.0000	0.8751			1.0000
+		1.0000	0.6990			1.0000
dC/dt	C_im	1.0000	0.8751			1.0000
+		-1.0000	0.6990			1.0000

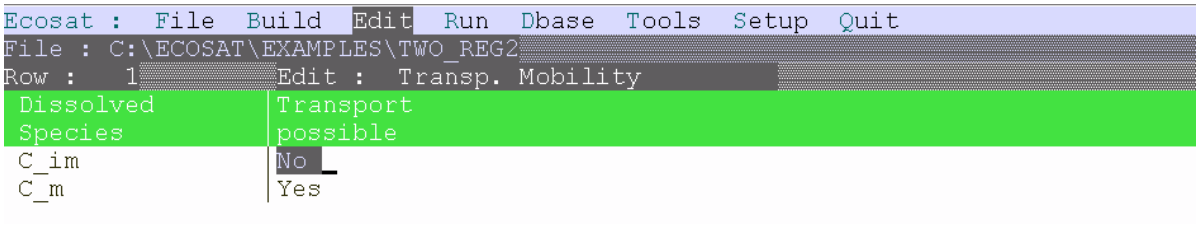
Kinetics – rate equations edit table continued :



In the first row of this table we have formulated the term ($-\alpha/\theta_m\ C_m$) of equation 11, with $\log(\alpha/\theta_m) = \log(1.5/0.2) = 0.8751 = K_1$. The second row represents the second kinetic term of equation 11, ($+\alpha/\theta_{im}\ C'_{im}$) with $\log(+\alpha/\theta_{im}) = \log(1.5/0.3) = 0.699$. In the third and fourth row the kinetic terms of equation 12 are formulated.

Transport - mobility table:

All transport and soil column data are inserted in the transport edit tables (parameters, soil column and feed). Finally, we have to inform ECOSAT that the dissolved species C_{im} is immobile. We can do this by choosing menu option **Transport - mobility**. ECOSAT then shows a list of all dissolved species. In this table we can indicate whether a species is mobile or not.

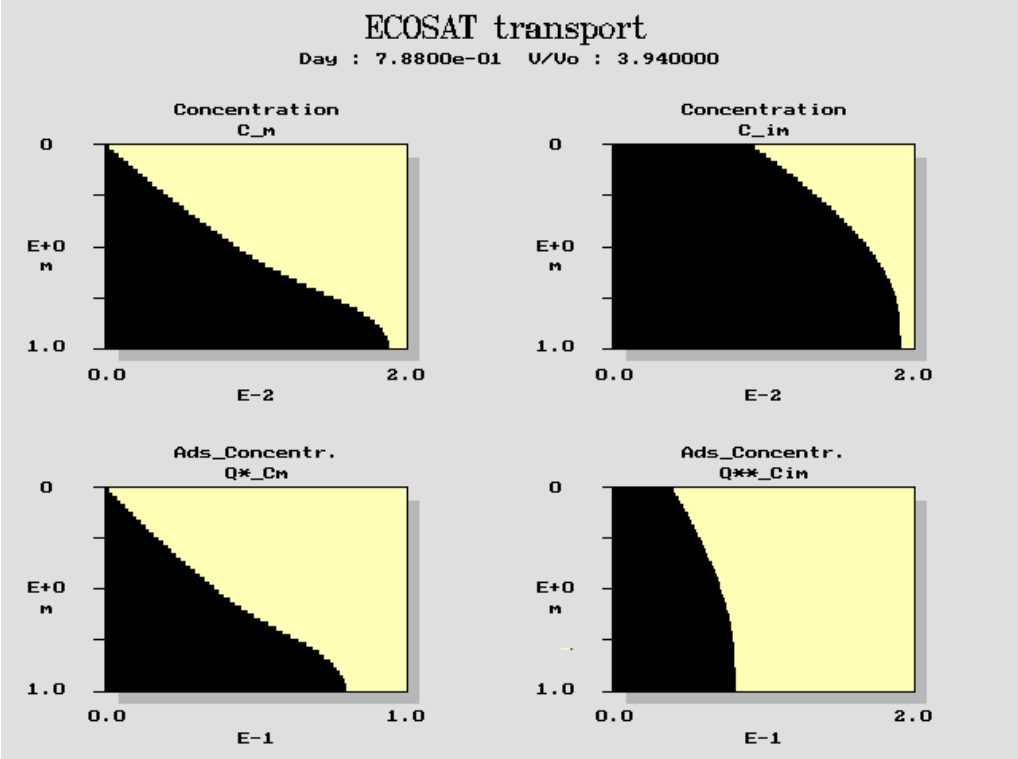


We remark that for gas flow we need not to use this option because only gas species are mobile then and not dissolved species.

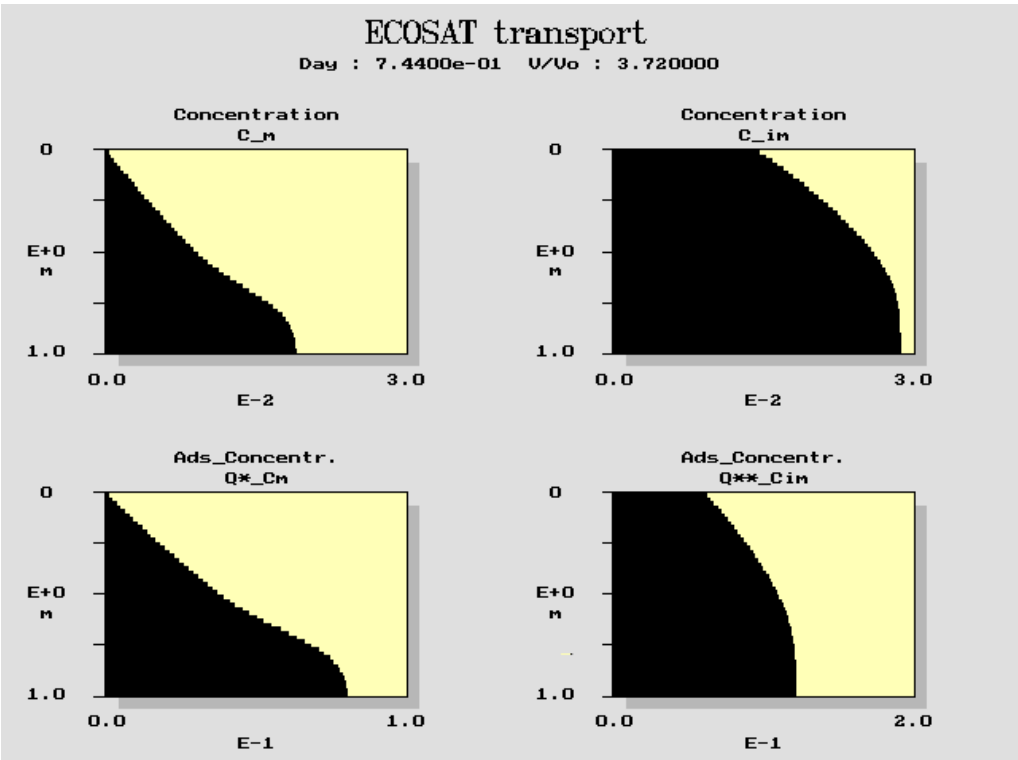
If you want to express C_{im} in mol/l immobile water you have to change the data for the total amount of component $C_{im,T}$ (Transport - Components) and the constants in the rate equations (Kinetics - Rate Equations. See example file TWO_REG1.eco.

In the following 2 ECOSAT screen dumps you see the calculated result of both approaches in the form of diagrams for the concentration profiles (see also VIEW, chapter 2.1.13). Note the difference for the concentration and adsorbed amount of C_{im}.

Concentration profile for file TWO_REG1



Concentration profile for file TWO_REG2



Two-site kinetic model.

In the two-site kinetic model, Parker and Van Genuchten (1984) assume two different types of adsorption sites. For one type of the sites adsorption will take place instantaneously and for the other type adsorption is rate limiting. Since the surface species belonging to this rate limiting adsorption are not in chemical equilibrium with the rest of the system, we have to define additional components for these species. Table 2.1. describes the two-site kinetic model that is used in Gaber et al. (1995).

TABLE 2.1 Table of species belonging to a simple two-site kinetic model

components	C	Q_S_2	log(K)
species			
C	1		0
Q_S_1	1		0.15
Q_S_2		1	0
total amount C_T (mol/l)	0.1	0.0944	

In this table of species we have defined a compound C which can adsorb onto two different sites. The total amount of Q_S_2 corresponds to the amount of the compound C that is initially adsorbed onto the slow reacting surface sites (S_2). Since Q_S_2 is not in chemical equilibrium with C, Q_S_2 is also used as component. For the fast reacting surface sites (S_1) a linear Freundlich isotherm is chosen. However, we may choose also a non-linear Freundlich equation. Other sorption models are not possible due to the fact that it has to be possible to calculate the adsorbed amount at equilibrium at any time step independent of the concentrations of all other components.

For the fast reacting surface sites a linear Freundlich isotherm is chosen: $S_1 = F.K_d.C$

For the equilibrium situation we use for S_2 the same model as for S_1: $S_{2,eq} = (1-F).K_d.C$

with $S = S_1 + S_2 = FS + (1-F)S$

Here we can only choose for the Freundlich model because the equilibrium situation ($S_{2,eq}$) has to be calculated independently from the actual composition of the system. It is possible to include components which concentration is not influenced by the sorption process in the formulation for $S_{2,eq}$ (e.g. pH-dependent Freundlich).

The slow mass transfer equation can be formulated as: $\frac{\partial S_2}{\partial t} = \mathrm{K_r}\left(S_{2,eq} - S_2\right)$

(15)

with S_s the total amount of the component on the slow ad/desorbing sites:

$S_2 = (1-F).K_d.C$ (mol/kg)
(16)

with F the fraction fast reacting sites.
K_d the distribution constant (l/kg).
K_r is the mass transfer rate constant (d^{-1}).

The governing equations for this two-site kinetic model are:

$$\frac{\partial C_T}{\partial t} = (1 + \frac{\mathrm{F}\rho \mathrm{K_d}}{\theta})\frac{\partial C}{\partial t} + \frac{\rho}{\theta}\frac{\partial S_2}{\partial t} = -\mathrm{v}\frac{\partial C}{\partial x} + \mathrm{D}\frac{\partial^2 C}{\partial x^2} = L(C) \tag{17}$$

$$\frac{\partial S_2}{\partial t} = \mathrm{K_r}\left[(1-\mathrm{F})\mathrm{K_d}C - S_2\right] \tag{18}$$

This system is represented schematically in figure 2.1.

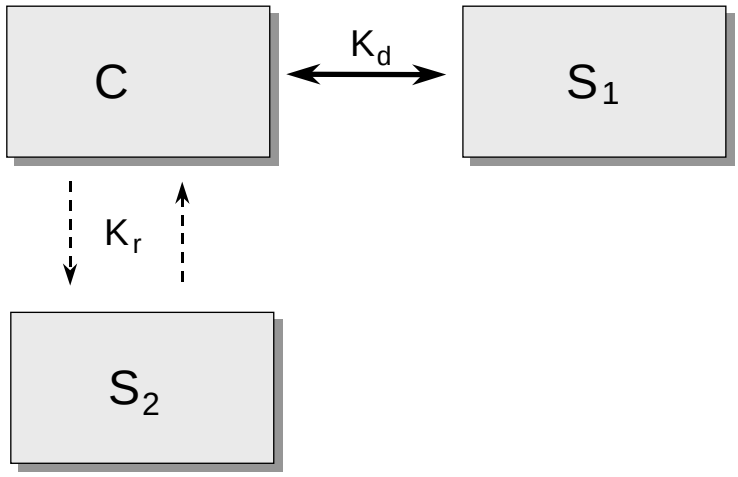


Figure 2.1. Schematic representation of the concept upon which the two-site model is based.

We will now rewrite equation 17 and 18 in a formulation that is used in ECOSAT. Substitution of equation 18 into 17 and rewriting the kinetic part gives:

$$\frac{\partial C_T}{\partial t} = L(C) - \frac{\rho}{\theta_v}\mathrm{K_r}(1-\mathrm{F})\mathrm{K_d}C + \frac{\rho}{\theta_v}\mathrm{K_r}S_2 \tag{19}$$

$$\frac{\partial S_2}{\partial t} = \mathrm{K_r}(1-\mathrm{F})\mathrm{K_d}C - \mathrm{K_r}S_2 \tag{20}$$

Note that the unit of S_2 is in mol/kg. Using the transformation $S_2^{'} = \frac{\rho}{\theta} S_2$ it is expressed in mol/l soil water. We then get:

$$\frac{\partial C_T}{\partial t} = L(C) - \frac{\rho}{\theta_v} \mathrm{K_r}(1-\mathrm{F})\mathrm{K_d}C + \mathrm{K_r}S_2^{'} = L(C) - \mathrm{k_1}C + \mathrm{k_2}S_2^{'}$$

(21)

$$\frac{\partial S_2^{'}}{\partial t} = \frac{\rho}{\theta_v} \mathrm{K_r}(1-\mathrm{F})\mathrm{K_d}C - \mathrm{K_r}S_2^{'} = \mathrm{k_1}C - \mathrm{k_2}S_2^{'}$$

(22)

Now we will show were to fill in the data into ECOSAT for this model. The data we will use are given in tables 2.1 and 2.2 (see also example TWO_SITE).

Table 2.2 Speciation and transport data for the two-site kinetic model

Soil column data	
ρ (soil bulk density) in kg/l soil	1.5
θ (volumetric water content)	0.5
L (column length) m	1
C_T (initial total amount) mol/l water	0.1
Q_$S_{2,T}$ (initial total amount) mol/l water	0.0944
Sorption data	
F (fraction of instantaneously adsorbing sites)	0.4
log K_{Fr} (Freundlich equilibrium constant)	0.15
n (Freundlich exponent)	1
K_r (sorption rate constant) d^{-1}	1.5
Transport data	
v_D (Darcy flux) m/d	1.0
D (diffusion /dispersion coefficient) m^2/d	0.005
Feed concentration in mol/l water	0

Components edit table:

Ecosat : File Build Edit Run Dbase Tools Setup Quit
File : C:\ECOSAT\EXAMPLES\TWO_SITE
Row : 4 ; Edit : Components More -->

Name comp.	Charge comp.	Constant Calc. Data type	Total amount (mol/l)	(Estimated) log(Conc./Act.)	Molar mass (g/mol)
C	0	Total amount	1.0000000E-01	-1.000000	1.0000
Q_S2	0	Total amount	9.4400000E-02	-1.000000	1.0000

The total amount of C is 0.1 mol / l mobile water. The total amount for Q_S_2 in the system has been calculated from the total amount for C assuming equilibrium at time 0. First calculate [C] for C_T = 0.1 mol/l: C_T=[C] + [Q_S_1] = [C] + Fρ.K_d.[C]/θ $\rightarrow$ [C] = 0.1/2.695 = 0.03711. Then calculate the concentration of Q_S_2: [Q_S_2] = (1-F)ρ.K_d.[C]/θ (mol/l) = 0.6 x 1.5 x $10^{0.15}$ x 0.03711/0.5 = 0.0944 mol/l.

Species edit table:

Ecosat : File Build Edit Run Dbase Tools Setup Quit
File : C:\ECOSAT\EXAMPLES\TWO_SITE
Row : 4 ; Edit : Species More -->

Name species	log(Ko) (298.15 K)	delta H kJ/mol	Molar mass **********	Reference comment	Coeff.
C	0.0000	0.0000	1.0000		1.0000
Q_S2	0.0000	0.0000	1.0000		1.0000

Species edit table continued:

Ecosat : File Build Edit Run Dbase Tools Setup Quit
File : C:\ECOSAT\EXAMPLES\TWO_SITE
Row : 4 ; Edit : Species More -->

delta H kJ/mol	Molar mass **********	Reference comment	Coeff.	Comp.	Coeff.	Comp.
0.0000	1.0000		1.0000	C		
0.0000	1.0000		1.0000	Q_S2		

Here, we have chosen for Q_S_2 as a dissolved species. This makes it easier because we do not have to specify a particular adsorption model for Q_S_2. Since we define Q_S_2 as a dissolved species we have to specify later that Q_S_2 is not mobile.

Particle surfaces edit table:

Adsorption : Particle surfaces Surface sorption Qo Interactions Quit
File : C:\ECOSAT\EXAMPLES\TWO_SITE
Row : 3 ; Edit : Particle surfaces More -->

Particle Surface	Particle Type	Related Mineral	Total amount (kg/l)	Sorption model	Geometry **********
Q	Solid		1.2000E+00	Freundlich	-

Note that we have to fill in the data for only one particle surface. The total amount of the particle surface belonging to the kinetic adsorption is accounted for in the total amount of Q_S_2.

Freundlich surface species table:

Adsorption : Particle surfaces Surface sorption Qo Interactions Quit
Particle surface : Q
Row : 3 ; Edit : Freundlich surface species More -->

Surface species	log(K-Fr) (at T)	Reference comment	Coeff.	Sorbed Comp.	Coeff.	Comp.
Q_S1	0.1500		1.0000	C		

The surface species Q_S_2 is already defined in the dissolved species table. So, in the **Freundlich surface species table** we have to define only the equilibrium surface species (Q_S_1). The soil solution ratio equals ρ^*/θ = 0.4 x 1.5/0.5 = 1.2 kg/l.

Kinetic - rate-equations edit table:

Ecosat : File Build Edit Run Dbase Tools Setup Quit
File : C:\ECOSAT\EXAMPLES\TWO_SITE
Row : 6 ; Edit : Kinetics - Rate equations More -->

dC/dt or +	Comp. (C)	Transfer Coeff.	Rate const. log(Kr)	Arrhenius -Ea/R	Arrhenius log(A)	Order
dC/dt	C	-1.0000	0.5814			1.0000
+		1.0000	0.1761			1.0000
dC/dt	Q_S2	1.0000	0.5814			1.0000
+		-1.0000	0.1761			1.0000

Kinetic - rate-equations edit table continued:

Ecosat : File Build Edit Run Dbase Tools Setup Quit
File : C:\ECOSAT\EXAMPLES\TWO_SITE
Row : 6 ; Edit : Kinetics - Rate equations More -->

Arrhenius log(A)	Order	Compound	Group/Part.Surf. **********	Order	Compound
	1.0000	C	species		
	1.0000	Q_S2	species		
	1.0000	C	species		
	1.0000	Q_S2	species		

In the first row of this table we have formulated the term ($-\rho/\theta\ k_2(1\text{-}F)\ K_d\ c_m$) of equation 21, with $\log(\rho/\theta_v\ k_2(1\text{-}F)\ K_d)$ = 0.5814. The second row represents the second kinetic term of equation 21, ($k_2 S$), with $\log(k_2)$ = 0.1761. In the third and fourth row the kinetic terms of equation 22 are formulated.

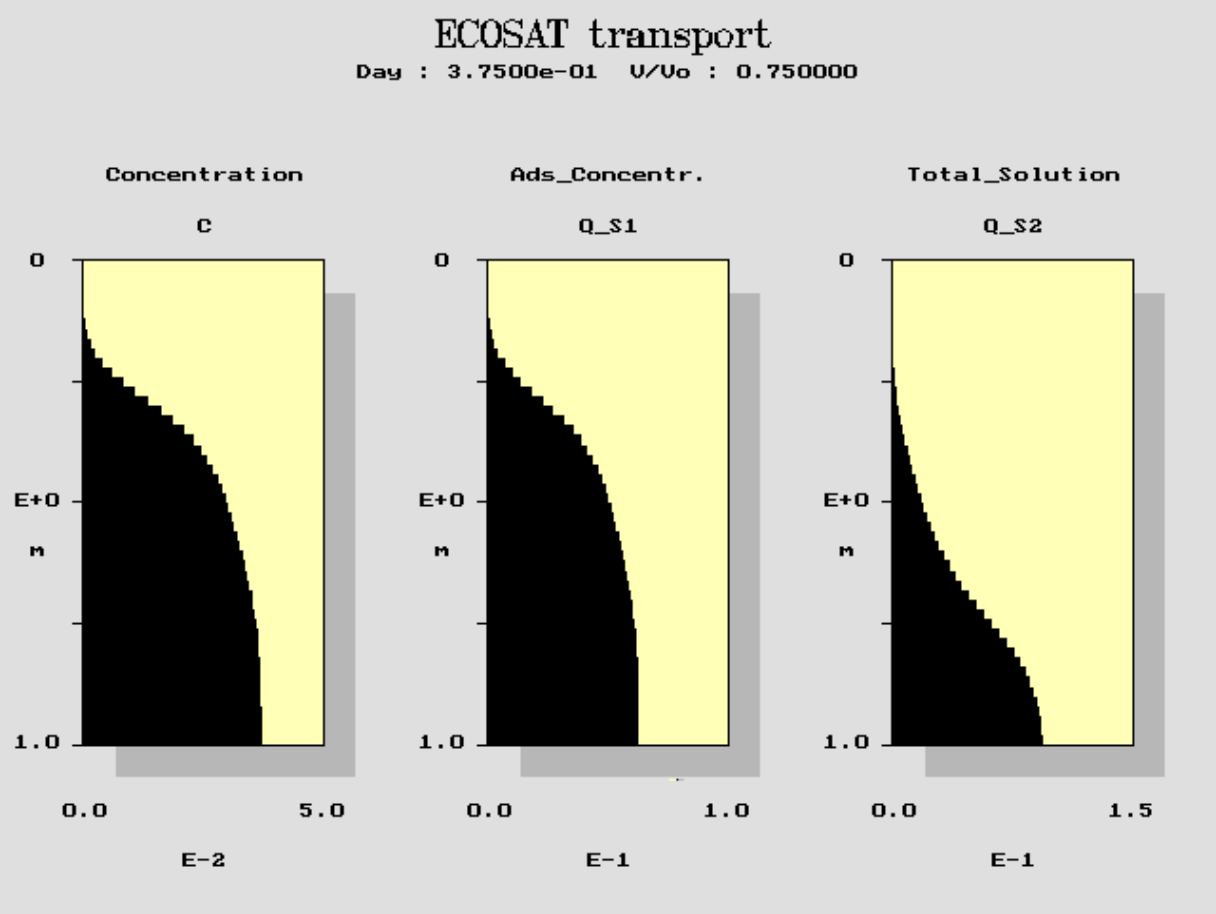
Transport - mobility edit table :

Finally, we have to inform ECOSAT that the species Q_S_2 is immobile:

Ecosat : File Build Edit Run Dbase Tools Setup Quit
File : C:\ECOSAT\EXAMPLES\TWO_SITE
Row : 2 Edit : Transp. Mobility

Dissolved Species	Transport possible
C	Yes
Q_S2	No

Concentration profile for file TWO_SITE



References:

Gaber, H.M., W.P. Inskeep, S.D. Comfort and J.M Wraith, Nonequilibrium transport of atrazine through large intact soil cores, Soil Sci. Soc. Am. J. 59:60-67, 1995

Parker, J.C., M.Th. van Genuchten, Determining transport parameters from laboratory and field tracer experiments. Virginia Agric. Exp. Stn. Bull. no 84-3.

Appendix 5

Semi-2D and Semi-3D transport in ECOSAT

Semi-2D and semi-3D transport in ECOSAT

General introduction

The formulation of the continuity equation, which is the basis for description of mass transport in soils, is given in general terms by:

$$\frac{\partial C}{\partial t} = -(\nabla . vC) + (\nabla . D\nabla C)$$

C: concentration

D: diffusion/dispersion coefficient
v: local pore velocity
t: time

In this equation we make use of the vector operations div (divergence) and grad (gradient). These vector operations are normally used for right Cartesian coordinates:

$$grad\varphi = \nabla\varphi = \left(\frac{\partial\varphi}{\partial x}, \frac{\partial\varphi}{\partial x}, \frac{\partial\varphi}{\partial x}\right)$$

$$div\ v = (\nabla . v) = \left(\frac{\partial v_1}{\partial x} + \frac{\partial v_2}{\partial y} + \frac{\partial v_3}{\partial z}\right)$$

The continuity equation can also be formulated in other coordinates like for instance cylindrical or spherical coordinates. For mass transport where we can neglect diffusion/dispersion it is rather easy to apply coordinate transformation using streamlines and equipotential lines. Also if only transversal diffusion/dispersion can be neglected 2- or 3-dimensional transport can be simplified using coordinates transformation.

In this way mass transport can be calculated along a streamline (1-dimensional flow), assuming no interactions with other streamlines (no mass transfer between streamlines).

Mathematical formulation

Assume: x = x(u,v,w)
y = y(u,v,w)
z = z(u,v,w)

A good view to the (u,v,w) coordinates offer the coordinate surfaces u = u_1 = constant, v = v_1 = constant, w = w_1 = constant and the coordinate curves $\underline{x}$ = $\underline{x}(u,v_1,w_1)$, $\underline{x}$ = $\underline{x}(u_1,v,w_1)$ and $\underline{x}$ = $\underline{x}(u_1,v_1,w)$.Each time two coordinates are kept constant. $\underline{x}$ equals a certain vector function.

The 3 coordinate curves have as tangents respectively : $\frac{\partial \underline{x}}{\partial u}, \frac{\partial \underline{x}}{\partial v}, \frac{\partial \underline{x}}{\partial w}$

The vectors $\frac{\partial \underline{x}}{\partial u}, \frac{\partial \underline{x}}{\partial v}, \frac{\partial \underline{x}}{\partial w}$ are in general no unity vectors. The length of these vectors equal to the scaling factors (h_1, h_2, h_3) :

$$h_1 = \left|\frac{\partial \underline{x}}{\partial u}\right|, \quad h_2 = \left|\frac{\partial \underline{x}}{\partial v}\right|, \quad h_3 = \left|\frac{\partial \underline{x}}{\partial w}\right|$$

We introduce now a new basis with unity vectors:

$$\underline{e_1} = \frac{1}{h_1}\frac{\partial \underline{x}}{\partial u},\quad \underline{e_2} = \frac{1}{h_2}\frac{\partial \underline{x}}{\partial v},\quad \underline{e_3} = \frac{1}{h_3}\frac{\partial \underline{x}}{\partial w}$$

In the new coordinate system with the basic vectors $\underline{e}_1$, $\underline{e}_2$, $\underline{e}_3$ we can give a formulation for vector v (velocity)

$\underline{v} = v_u\underline{e}_1 + v_v\underline{e}_2 + v_w\underline{e}_3$

with

$$v_u = (v, \underline{e_1}) = \frac{1}{h_1}\left(\underline{v}, \frac{\partial \underline{x}}{\partial u}\right)$$

$$v_v = (\underline{v}, \underline{e_2}) = \frac{1}{h_2}\left(\underline{v}\frac{\partial \underline{x}}{\partial v}\right)$$

$$v_w = (\underline{v}, \underline{e_3}) = \frac{1}{h_3}\left(\underline{v}, \frac{\partial \underline{x}}{\partial w}\right)$$

Note that the scaling factors are not constants, but are a function of place.

In the coordinate system given by u, v, w the formula's for the vector operations div and grad are different from the formula's for the operators in the standard Cartesian coordinate system:

$$(\nabla.\underline{v}) = \frac{1}{h_1h_2h_3}\left(\frac{\partial\left(h_2h_3v_u\right)}{\partial u} + \frac{\partial\left(h_3h_1v_v\right)}{\partial v} + \frac{\partial\left(h_1h_2v_w\right)}{\partial w}\right)$$

$$(\nabla C) = \left(\frac{1}{h_1}\frac{\partial C}{\partial u},\ \frac{1}{h_2}\frac{\partial C}{\partial v},\ \frac{1}{h_3}\frac{\partial C}{\partial w}\right)$$

Transport equation in cylindrical coordinates

2-or 3-dimensional mass transport with axial symmetrical (cylindrical) flow can be transformed to 1-dimensional flow using cylindrical coordinates.

If transversal diffusion/dispersion can be neglected the solution of the mass transport problem only depends on the distance to the line source (radius of the cylinder).

Introducing cylindrical coordinates (r,φ,z) we can solve this 3-dimensional problem in 1-D (in the r-direction). De cylindrical coordinates (r,φ,z) depend on the Cartesian coordinates (x,y,z) according to

$x = r.\cos\varphi,\qquad y = r.\sin\varphi,\qquad z = z$ (r = radius of the cylinder)

The scaling factors belonging to this transformation are:

$h_1 = 1,\ h_2 = r,\ h_3 = 1$

Continuity equation:

$$\frac{\partial C}{\partial t} = -(\nabla.\underline{v}C) + (\nabla.D\nabla C) = -C(\nabla.\underline{v}) - (\underline{v}.\nabla C) + (\nabla.D\nabla C)$$

If there is no divergence, (∇.$\underline{v}$)=0 and if D depends only on r:

$$\frac{\partial C}{\partial t} = -(\nabla.\underline{v}C) + (\nabla.D(r)\nabla_r C) \qquad \text{with v and D as function of r.}$$

$$\frac{\partial C}{\partial t} = -v(r)\frac{\partial C}{\partial r} + \frac{1}{r}\frac{\partial}{\partial r}rD(r)\frac{\partial C}{\partial r}$$

The data for the flux, v(r), and for the scaling factors, h_1, h_2, h_3 have to be given in a data file (*.s2D or *.s3D).

Example cylindrical flow (v = 1 at r = 1.0 (node 0)):

node	**v**	**h_1**	**h_2**	**h_3**
1	1,11	1	0,9	1
2	1,25	1	0,8	1
3	1,43	1	0,7	1
4	1,67	1	0,6	1
5	2	1	0,5	1
6	2,5	1	0,4	1
7	3,33	1	0,3	1
8	5	1	0,2	1
9	10	1	0,1	1
10	100	1	0,01	1

At r=0 we take a small value for r (otherwise zero division).

Available pore volume for flow (water content or gas content) can also be a function of r. In that case add an extra column for θ.

For radial symmetric (spherical) flow we get a more or less equal approach.
Scaling factors are then: $h_1 = 1$; $h_2 = r$ and $h_3 = r \sin\varphi$.

Mass transport equation in pole coordinates

Knowing streamlines and equipotential surfaces, the transport problem can be solved in a coordinates system determined by these streamlines and potential surfaces (Bear and Verruyt,1987). If diffusion/dispersion can be neglected we can solve the transport problem along the streamlines.
Note: no diffusion/dispersion at all !

If only transversal diffusion/dispersion can be neglected we have to know the scaling factors for all nodes. They have to be derived numerically from flow data.

Introducing the potential coordinates (ξ, θ, φ) we can solve this 3D-problem in 1D (in the flow direction or ξ-direction). The potential coordinates (ξ, θ, φ) are a function of the Cartesian coordinates (x, y, z) :

$$x = f_1(\xi,\theta,\varphi)$$
$$y = f_2(\xi,\theta,\varphi)$$
$$z = f_3(\xi,\theta,\varphi)$$

The scaling factors belonging to this transformation are:

$$h_1 = \left|\left(\frac{\partial f_1}{\partial \xi},\frac{\partial f_2}{\partial \xi},\frac{\partial f_3}{\partial \xi}\right)\right|$$
$$h_2 = \left|\left(\frac{\partial f_1}{\partial \theta},\frac{\partial f_2}{\partial \theta},\frac{\partial f_3}{\partial \theta}\right)\right|$$
$$h_3 = \left|\left(\frac{\partial f_1}{\partial \varphi},\frac{\partial f_2}{\partial \varphi},\frac{\partial f_3}{\partial \varphi}\right)\right|$$

Conservation equation:

$$\frac{\partial C}{\partial t} = -(\nabla.\underline{v}C) + (\nabla.D\nabla C) = -C(\nabla.\underline{v}) - (\underline{v}.\nabla C) + (\nabla.D\nabla C)$$

If there is no divergence, (∇.v) = 0 and diffusion/dispersion can be neglected:

$$\frac{\partial C}{\partial t} = -(\underline{v}.\nabla C) \qquad \text{with} \qquad \underline{v} = \left(v(\xi),0,0\right)$$

If the coordinates in the ξ-direction are equidistant, than the scaling factor h_1 equals 1:

$$\frac{\partial C}{\partial t} = -v(\xi)\frac{\partial C}{\partial \xi}$$

Note that in this case the values of the other scaling factors are not important (no diffusion/dispersion).

Appendix 6

Examples

How to run example files

Example files (*.eco) can be found in subdirectory .\ecosat\examples. To run an example file start ECOSAT (eco) and choose FILE - RETRIEVE and select the specific file. Inspect the edit tables to learn and press RUN to start the calculation. Sometimes a specific selections output file (*.sof) is available. This file is automatically retrieved by the Output manager and can be used to generate output. If there is no specific selections output file you can make your own output with option CHOICE or use option BASIC or ALL. Output is stored in file outman.dat.

Examples overview

ADS_FR.eco
Adsorption of Cd according to a pH-dependent Freundlich model and a linear model on two particle surfaces. Complexation of Cd with Cl and hydrolysis of Cd. Variable ionic strength and pH variation in a multiple run calculation (= adsorption edge).
Output: ADS_FR.sof

ADS_LANG.eco
Adsorption of Cd according to the Langmuir model (nvc). Complexation of Cd with Cl and hydrolysis of Cd. Constant pH and ionic strength. Multiple run calculation for total amount of Cd (= adsorption isotherm).
Output: ADS_LANG.sof

AlOH.eco
Al-hydrolysis: multiple run calculation for pH.

ADSLAADV.eco
Adsorption of Cd according to the Langmuir Advanced model. Multiple run calculation for Cd total amount.
Output: ADSLAADV.sof

AXIALS2D.eco
Transport of chloride by semi-2-dimensional water flow (axial symmetric). Flux data and scaling factors in file axials2d.s2d. View diagram of total amount of Cl in the soil column.
Output: AXIALS2D.sof (breakthrough curve of Cl at several nodes).

BTX.eco
Speciation for a mixture of organic liquids: benzene, toluene and xylene. Adsorption onto organic matter according to a linear (Freundlich) model.

BT_VENT.eco
Transport of benzene and toluene via the gas phase (venting). Speciation: organic liquids, gases, dissolved and adsorbed. View diagrams for total amounts of benzene and toluene in gas phase, organic liquid phase and adsorbed.

CASCADE.eco
Repeated $CaCl_2$-extraction (=cascade treatment) of soil containing Cd and Zn. Adsorption of Cd and Zn according to a pH-dependent Freundlich model. Constant pH and variable ionic strength.
Output: CASCADE.sof

CDCL.eco
Complexation of Cd with Cl and hydrolysis. Variable pH and constant ionic strength.

CDCL_FIT.eco
Complexation of Cd with Cl. Fit parameter choice for $\log(K^0)$ of a dissolved species ($CdCl^-$). Multiple run calculation for Cl total amount.
Output: CDCL_FIT.sof

CD-NICA.eco
Cd-adsorption according to the NICA non variable charge model.

CL_BTC.eco
Calculation of the breakthrough curve for Cl. Output time data from file CL_BTC.tof.
View diagram for total amount of chloride in solution.
Output: CL_BTC.sof

CO2.eco
Cd speciation: complexation with Cl and CO_3, hydrolysis. Constant pH and variable ionic strength. Constant gas pressure for CO_2 in a multiple run calculation.
Output: CO2.sof

Cu-Multi.eco
Multi site complexation for Cu in clay soil. Particle surfaces: SOM, DOM, Clay; Components: Cu, Ca, Al, NO_3, H and OH. Sorption models: NICA-Donnan for SOM and DOM, Donnan ion exchange for clay (illite). Al in equilibrium with gibbsite; constant Ca concentration.

CYANIDE.eco
Cyanide speciation: dissolved $Fe(CN)_6$-species and equilibrium with Prusian blue and ironhydroxide. Constant pH in a multiple run calculation. Constant ionic strength. Electron as component.
Output: CYANIDE.sof

Delta-H.eco
CO_2-H_2O-$CaCO_3$(s) system with temperature variation in multiple run.

DonnanIE.eco
Donnan ion exchange (nvc-model) for clay. Particle surface: clay (illite); Components: Cu, Ca, NO_3, H and OH. Donnan volume = 0.1 L for clay; constant Ca concentration.

FEOH_KIN.eco
Slow dissolution of $Fe(OH)_3$ (s). Fe-hydrolysis, variable pH, constant ionic strength. View diagrams for total amount and log(IAP) of $Fe(OH)_3$ (s).

FLUOR.eco
Adsorption of F onto goethite according to the Basic Stern model (VC - Langmuir Normal - Plane - BS). Constant ionic strength and multiple run for pH.
Output: FLUOR.sof

IONSTR.eco
Calculation of ionic strength.

ION_EXCH.eco
Na-Ca exchange with Gaines-Thomas model. Multiple run calculation for Ca total amount.

KIN_BT.eco
Decay of benzene - toluene organic liquid mixture (decay only in the water phase). Speciation: organic liquid, gas, dissolved and adsorbed (linear model). View diagrams for total amounts of benzene and toluene in all phases.

MIN-NICA.eco
Combination of adsorption according to the VC-NICA Donnan model and precipitation of minerals. Constant pH and constant pe in multiple run calculation.

MINERALS.eco
Speciation of Cd, Ca and CO_3 : formation of precipitates (carbonates, hydroxides). Constant CO_2-pressure, constant pH, variable ionic strength.

MnOH_KIN.eco
Slow dissolution of MnO_2 (s). Variable pH, constant ionic strength. View diagrams for total amount and log(IAP) of MnO_2 (s).

NACA_EXCH.eco
Transport of Ca and Na in the soil. Ion exchange according to Gaines-Thomas. First leaching of Ca in a Na-soil, followed by leaching of Na in the Ca-soil (after 3 pore volumes of leaching).
View diagrams with Na and Ca total amounts in solid and water phase.

NICA_TES.eco
Adsorption of many heavy metals onto DOM (GFA and GHA) using NICA-DONNAN model.

NICA-2CD.eco
Sorption of Cd and H onto humic acid (GHA) according to NICA-Donnan model. Gel volume as function of ionic strength. Variable ionic strength and multiple run for pH and Cd-concentration.
Output: NICA-2CD.sof

NICA-2DH.eco
Sorption of H onto humic acid (GHA) according to NICA-Donnan. Initially adsorbed amount (Q_o) for H. Multiple run for background electrolyte (K, NO_3, and added base (NaOH): Na and OH). Gel volume function of ionic strength; variable ionic strength.
Fitting parameter: Q_o of H.
Output: NICA-2DH.sof

NICA_CD.eco
Sorption of Cd and H onto humic acid (GHA). Multiple run for Cd-total amount and pH read from data file (*.mrf). Fitting parameters: several parameters for surface species. Variable ionic strength. Gel volume function of ionic strength.
Output: NICA_CD.sof

NICA_DH.eco
Sorption of H onto humic acid (GHA). Multiple run for pH read from data file (*.mrf). Fit parameter choice for Q_o-H, surface components and surface species. Variable ionic strength. Gel volume function of ionic strength. Initially adsorbed amount (Q_o) for H.
Output: NICA_DH.sof

NICA_DON.eco
Adsorption of H and Ca onto humic and fulvic acid according to the NICA-Donnan model. Variable gel volume as function of ionic strength, variable ionic strength; Multiple run for Ca- and H-concentration.
Output: NICA_DON.sof

RADIALS3D.eco
Transport of chloride by semi-3-dimensional water flow (radial symmetric). Flux data and scaling factors in file radials3d.s3d. View diagram of total amount of Cl in the soil column.
Output: RADIALS3D.sof (breakthrough curve of Cl at several nodes).

REL_MIN.eco
Zn-adsorption on Fe-oxide particle surface according to Freundlich model. Total amount of Fe-oxide equal to calculated amount of goethite (= related mineral). Variable pH and constant ionic strength.

SPM_TRAN.eco
Transport of zinc via 1-dimensional water flow. Adsorption of Zn according to the SPM-model.
View diagrams for solid solution formation, pH and Zn-total amount in different phases.
Solution not stable!

SPM_PLOT.eco
Adsorption of Zn according to the SPM-model. Multiple run for Zn-concentration. Constant pH and constant ionic strength.
Output: SPM_PLOT.sof

TRA_ATRA.eco
Transport of atrazine combined with slow desorption according to the 2-site kinetic model.
View diagrams of fast and slow reacting atrazine.

TRA_CD_H.eco
Transport of Cd, H and DOC via 1-dimensional water flow. Adsorption of Cd onto soil and suspended DOC according a pH dependent Freundlich model.
View diagrams for total amounts of relevant compounds.

TRA_PO4.eco
Transport of phosphate via 1-D water flow. Adsorption of PO_4 on goethite according to the Tri-plane model (VC - Langmuir - Normal - Plane - Triple Layer).
View diagrams for phosphate in several phases.

TWO_REG1.eco
Transport combined with 2 region kinetic model. C_{im} expressed in mol/l immobile water.
View diagrams for total amount of the compound in the 2 regions.

TWO_REG2.eco
Transport combined with 2 region kinetic model. C_{im} expressed in mol/l mobile water.
View diagrams for total amount of the compound in the 2 regions.

TWO_SITE.eco
Transport combined with the 2-site kinetic model.
View diagrams for the compound in the 2 sites.